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Manganese Fuel Additive (MMT) Can Cause Vehicle Problems

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MOST OF THE CARS MANUFACTURED in the United States since 1975 require unleaded gasoline for satisfactory operation of catalytic converters used to control exhaust emissions. Consequently, the demand for unleaded gasoline is increasing each year as old cars are replaced with new converter-equipped cars. To meet this demand and to provide the desired octane quality, some petroleum refiners have begun using the antiknock additive methylcyclopentadienyl manganese tricarbonyl (MMT). MMT was developed by Ethyl Corporation in 1957 (1,2)* and was marketed initially as a fuel antiknock compound to supplement tetraethyllead. Recently, Ethyl evaluated MMT as a primary antiknock for unleaded gasoline (3) and concluded that for normal vehicle operation MMT is compatible with engines and emission control systems if used within the recommended concentration range (up to 0.033 grams of manganese per litre). However, they did find some adverse effects with monolithic catalysts and spark plugs in severe service. Others (4,5) have investigated the toxicological and environmental aspects of MMT and generally concluded that the use of MMT within the recommended concentration range would not result in any public health problems.

Since serious problems were not apparent with MMT, some of the petroleum companies started to use it in unleaded gasoline. In the MVMA National Fuel Survey for the Winter of 1976-77 (6), 45 of the 235 unleaded fuels which were sampled throughout the United States contained detectable amounts of manganese. The average manganese content of those 45 fuels was 0.009 g/ℓ (0.034 g/gal). Apparently many oil companies are currently using MMT to adjust the octane quality of gasoline at their refineries. As the demand for unleaded gasoline increases, it seems reasonable to expect that the use of MMT may also increase, both in terms of the volume of gasoline containing MMT and in the average concentration of manganese.

Since Ethyl's earlier work (3) suggested that MMT may cause problems in severe service, we evaluated two kinds of catalytic converter emission control systems for compatibility with

* Numbers in parentheses designate References at end of paper.

ABSTRACT

A manganese fuel additive, MMT, is now being used in many unleaded gasolines to improve their octane quality. Use of MMT at concentrations up to 0.033 g Mn/ℓ (0.125 g Mn/gal) is expected to increase. To determine the effect of MMT on exhaust emission control systems, five cars were tested for 80 000 km (50,000 miles) using a driving schedule which included 113 km/h (70 mph) steady speed driving. In this type of operation, use of MMT caused ... located close to the exhaust manifold; partial plugging of an underfloor bead converter; an increase of hydrocarbon emissions from the engines; and excessive spark plug deposits. However, use of MMT apparently enhanced catalytic converter oxidizing activity and did not substantially affect octane requirement increase. These preliminary data suggest that use of MMT in commercial gasolines may cause problems with exhaust emission control systems

MMT during service which was more severe than the Federal emission certification durability schedule. Results of our evaluation are presented in this paper. The experimental program will be described, and then catalyst plugging, exhaust emissions, fuel economy, and spark plug deposits will be discussed.

EXPERIMENTAL

Two 1976 Oldsmobile Cutlasses equipped with bead-type underfloor converters and three 1977 Chevrolet Novas equipped with monolithic manifold and bead-type underfloor converters accumulated mileage on chassis dynamometers using the R007 driving schedule (Appendix A) which was more severe than the emission certification schedule. One Cutlass and one Nova were fueled with the unleaded gasoline normally used for mileage accumulation during exhaust emission certification tests. The other three cars used the same base gasoline to which MMT was added at a concentration of 0.034 g Mn/ℓ (0.129 g Mn/gal). Some tests were also run on one car with the base gasoline containing 0.017 g Mn/ℓ (0.064 g Mn/gal). Four of the cars accumulated 80 000 km (50,000 miles), but tests were terminated on the other car at 64 000 km (40,000 miles) because of repeated plugging of the monolithic converter.

The fuels, cars, and test program are described in detail in Appendix A.

CATALYST PLUGGING

A major objective of this program was to determine whether the MMT combustion products would cause deposits that would plug catalytic converters. It was decided that a converter failure due to plugging would be based on driveability complaints from the vehicle operator during mileage accumulation, emission testing, or octane testing. Whenever a driveability complaint (such as rough idle or poor throttle response) was received, catalyst pressure drop and vehicle performance were measured to determine if the converter was plugged. If the pressure drop exceeded twice the original value for a new converter, the converter was judged to be plugged.

MONOLITHIC CONVERTER PLUGGING - The history of plugging of the close-coupled monolithic converters used on the Novas is summarized in Figure 1. One car, CH63291, plugged two monoliths consecutively with 1/8 MMT Fuel (0.034 g Mn/ℓ) and one with 1/16 MMT Fuel (0.017 g Mn/ℓ). With another car, CH63289, the monolith did not plug until the end of the test with 1/8 MMT Fuel. The monolith on the third car, CH63326, was not plugged at the end of the test; this car used Clear Fuel which did not contain manganese.

The degree of plugging of each monolith can be expressed in terms of the increase in pressure drop across the monolith as shown in Table 1. When the monolith plugged, the pressure drop increased from two to four times the value obtained with a new monolith. This restriction was accompanied by an increase in both wide-open-throttle (WOT) and part-throttle (PT) acceleration times as also shown in Table 1.

After monolith plugging was verified, or at the end of the program, the converters were removed for analysis. Photographs of the inlet surface of each of the monoliths tested are shown in Figure 2; a new monolith is also shown for comparison. Deposits had plugged many of the passages of each monolith which was exposed to MMT, reducing the effective cross sectional area available for exhaust gas flow. This restriction increased the pressure drop across the monolith and decreased vehicle performance as described previously. The monolith which was not exposed to MMT showed very little plugging and, therefore, pressure drop and performance were not appreciably affected.

WHY DID THE MONOLITHS PLUG? - The first monolith which plugged on car CH63291 was removed and analyzed to determine the plugging mechanism. Deposits were scraped from the inlet face of the leading section of the monolith. These reddish-brown deposits consisted primarily of manganese oxide (Mn_3O_4) with traces of elements from the catalyst washcoat and the engine lubricating oil. Both the

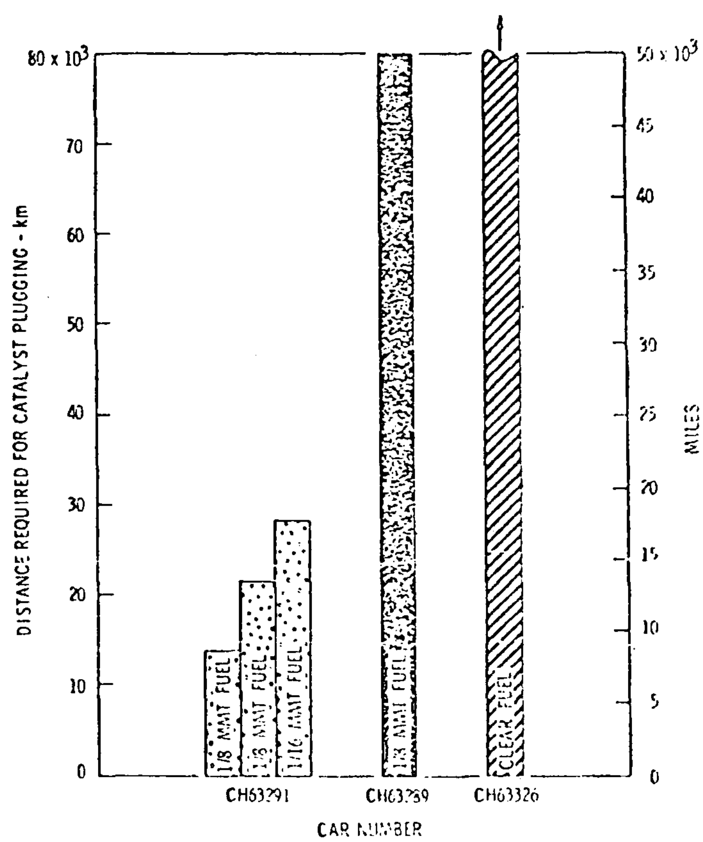


Fig. 1 - Plugging of close-coupled monoliths - 1977 Novas

Table 1 - Catalyst Pressure Drop and Vehicle Acceleration Performance - Novas

Car	Odometer km	Odometer (mi)	Fuel	Test Condition	Pressure Drop Across Monolith(1) kPa	Pressure Drop Across Monolith(1) (in. Hg)	Acceleration Time, sec WOT(2)	Acceleration Time, sec PT(3)	Engine Back Pressure (Absolute)(1) kPa	Engine Back Pressure (Absolute)(1) (in. Hg)
CH63291	13 679	(8,500)	1/8 MMT	Plugged Monolith #1	75.2	(22.2)	30.8	-	198.9	(58.75)
	35 665	(22,161)	1/8 MMT	Plugged Monolith #2	48.1	(14.2)	25.4	-	178.3	(52.65)
	64 482	(40,067)	1/16 MMT	Plugged Monolith #3	74.5	(22.0)	28.5	153.9	197.9	(58.46)
	64 683	(40,190)	1/16 MMT	Baseline(4)	15.9	(4.7)	21.6	47.5	132.8	(39.21)
CH63289	81 050	(50,362)	1/8 MMT	Plugged Monolith	37.9	(11.2)	23.9	69.7	170.0	(50.21)
	81 249	(50,486)	1/8 MMT	Baseline(4)	16.6	(4.9)	21.0	47.7	156.4	(46.20)
CH63326	80 557	(50,056)	Clear	End of Test	15.6	(4.6)	22.9	40.7	127.2	(37.57)
	80 767	(50,186)	Clear	Baseline(4)	18.3	(5.4)	22.9	41.4	131.2	(38.75)

(1) Wide-open throttle, 4000 rpm.
(2) Wide-open-throttle (WOT) acceleration, 0-98 km/h (0-60 mph).
(3) Part-throttle (PT) acceleration, 56-80 km/h (35-50 mph) at 20 kPa (6 in. Hg).
(4) Baseline tests with new monolith, new spark plugs.

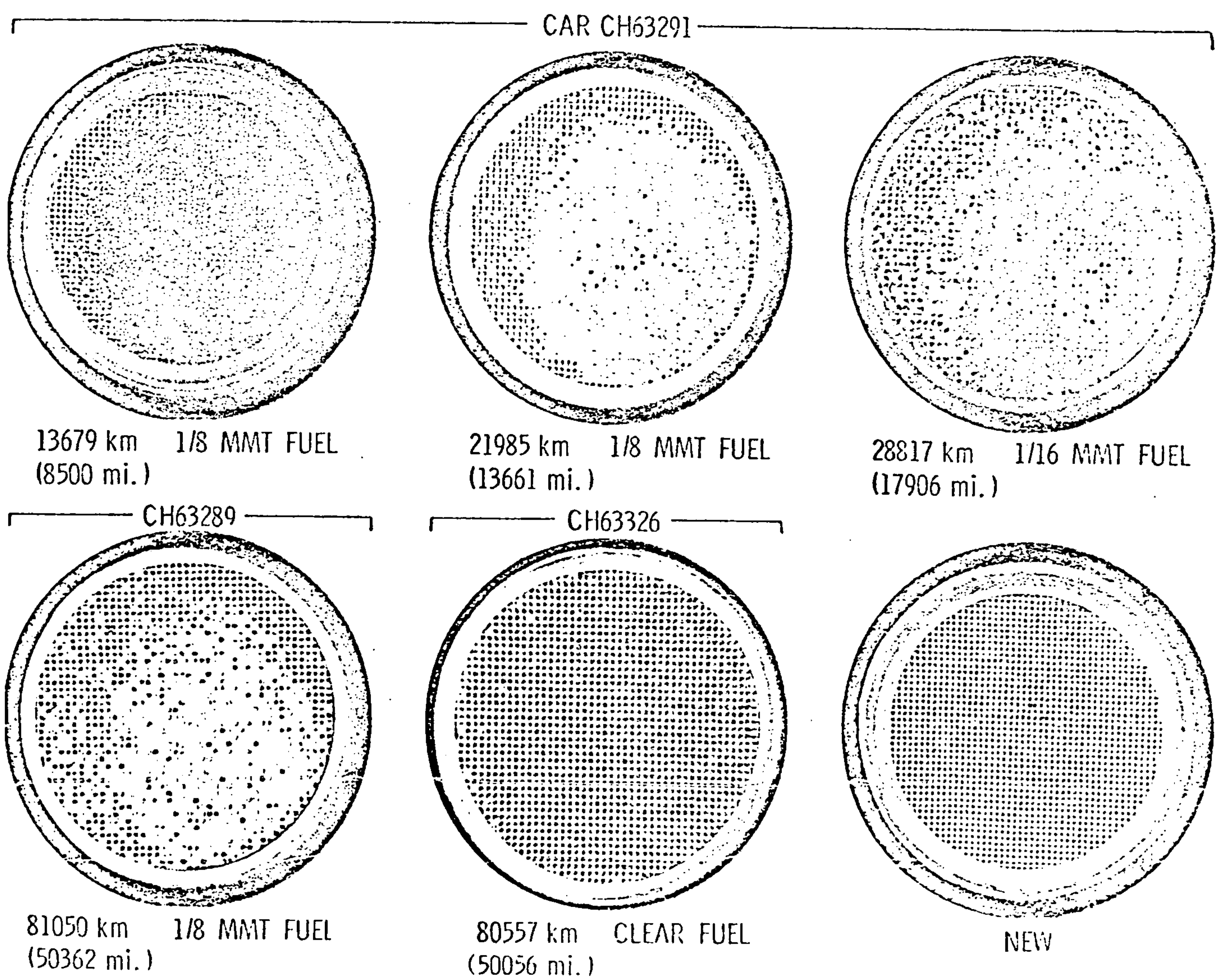
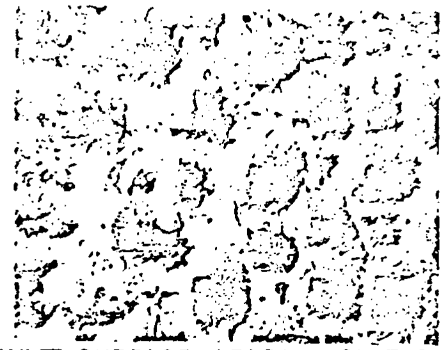


Fig. 2 - Inlet surface of close-coupled monolithic converters

leading and trailing portions of the monolith were sectioned axially (parallel to the exhaust channels). Photographs of these sections were taken through an optical microscope and are shown in Figure 3. These photographs show the deposit accumulation on the inlet surfaces of the leading and trailing sections of the monolith and a plug of deposits in one channel of the inlet section. This plug occurred at the inlet surface and was about 2 mm long. None of the channels in the trailing section were plugged, although Mn_3O_4 deposits were found along the entire length of the channels in both the leading and trailing sections of the monolith. An electron microprobe analysis of one of the monolith channels was also performed. There appeared to be three distinct layers: the manganese deposit in the top layer, the alumina washcoat in the center, and the silica substrate in the lower layer. There was no evidence of any chemical interaction between the manganese and the silica layers. This suggests that the deposit mechanism may be a physical one rather than a chemical reaction between manganese and silica to form silicates as had been proposed earlier during a meeting with researchers from Ethyl Corporation. Work is in progress at GM Research Laboratories to define the mechanism of plugging.

After establishing that the monolithic converter was plugged with Mn_3O_4 deposits, the next question was what caused the variation in plugging frequency? One car (CH63291) plugged monoliths more frequently than an identical car (CH63289) using the same fuel (1/8 MMT Fuel). One possible explanation might be a difference in exhaust gas temperature. Faggan, et al. (3), reported that 816°C (1500°F) was the threshold temperature for plugging of close-coupled monoliths as determined from engine dynamometer tests. In these tests, plugging was not encountered when exhaust temperatures at the monolith inlet were below 760°C (1400°F). To determine the exhaust temperature profile for each Nova, a thermocouple was installed in the exhaust manifold, and temperatures were measured on the dynamometer during the driving schedule. The thermocouple was located along the axis of the monolith; it was perpendicular to and 1.27 cm (0.5 in.) above the inlet surface.

Figure 4 shows the distribution of exhaust gas temperatures for each Nova. One car, CH63289, had substantially lower exhaust temperatures - 743°C (1370°F) maximum - than either of the other two cars. This car also went 81 000 km using 1/8 MMT Fuel before the monolith plugged. Car CH63291, which plugged three monoliths using fuel with MMT, experienced a maximum exhaust temperature of 843°C (1550°F) but exceeded 816°C (1500°F) less than 1 percent of the total driving time. These temperature measurements suggest that monolith



INLET SURFACE, LEADING SECTION

INLET SURFACE, TRAILING SECTION

PLUG OF DEPOSITS IN MONOLITH CHANNEL

Fig. 3 - Manganese deposits on monolith surfaces

threshold temperature level of 816°C (1500°F) since one car (CH63289) plugged a monolith at temperatures below the assumed threshold level. Furthermore, the data suggest that a combination of exhaust temperature and time of exposure at that temperature is important.

The reason for the spread in exhaust temperatures among the three cars shown in Figure 4 is unknown. Examination of compression ratio, spark advance, carburetor flow, and EGR flow data yielded no explanations since all three Novas were very closely matched with respect to initial calibrations.

Exhaust temperatures of these Novas were also measured on a level road at several different constant vehicle speeds ranging from 48

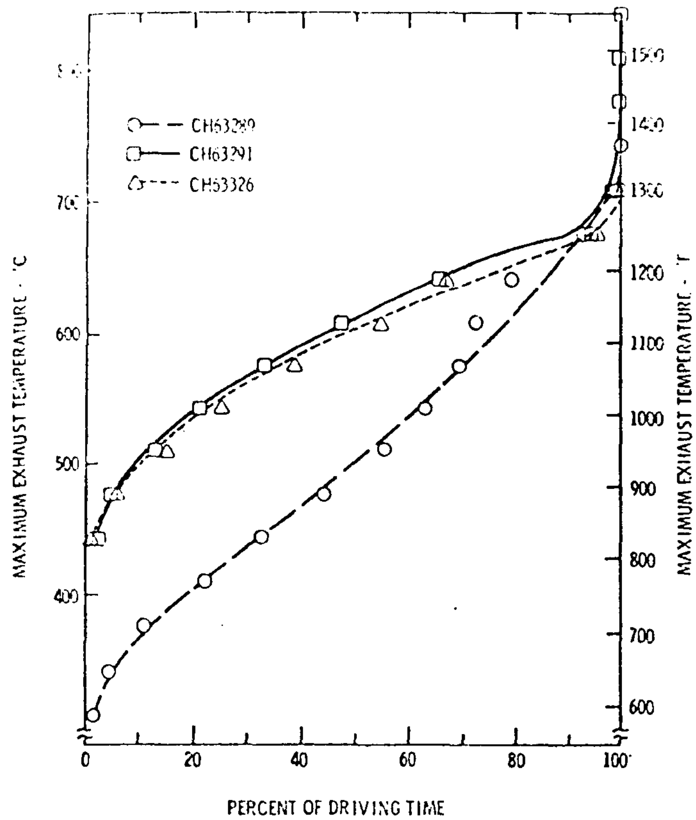


Fig. 4 - Distribution of exhaust gas temperatures at monolith inlet during R007D driving schedule - Novas

temperatures were also measured with four 1977 Caprices with the same engine and emission control systems. The Novas weighed 1 490 kg (3284 lbs) and the Caprices weighed 1 652 kg (3643 lbs). Exhaust temperatures are plotted in Figure 5. The three Novas had cooler exhaust temperatures than the four Caprices at low vehicle speeds, but at 113 km/h (70 mph) temperatures for all cars were between 760 and 788°C (1400 and 1450°F). Therefore, exhaust temperatures of the Novas were not atypical, and may have been cooler during the low speed portions of the driving cycle than those generated by the same engine in a heavier car. At low speeds, the engine must work harder in a heavier car to maintain constant power, but at 113 km/h the engine was operating at essentially full throttle in both the Novas and the Caprices.

These results suggest that if exhaust temperature and exposure time are the critical parameters, then cars with close-coupled monoliths may encounter plugging during operation with fuel containing MMT at a level of 0.017 g Mn/ℓ (0.064 g Mn/gal) or greater.

BEAD-TYPE CONVERTER PLUGGING - In addition to the monolith plugging which was observed with the Novas, some restriction of the underfloor bead-type converter was also found with one of the Cutlasses. Catalyst pressure drops and vehicle acceleration performance for the Cutlasses are summarized in Table 2. For car R6908 using 1/8 MMT Fuel, the catalyst pressure drop tripled and WOT acceleration time increased 2.5 seconds. For the other car (R6907) using Clear Fuel, neither catalyst pressure drop nor acceleration times changed significantly. Even though the back pressure increased 24 percent for car R6908, no driveability complaints were received. Apparently this car had a high enough power/weight ratio that the loss in performance was not particularly noticeable.

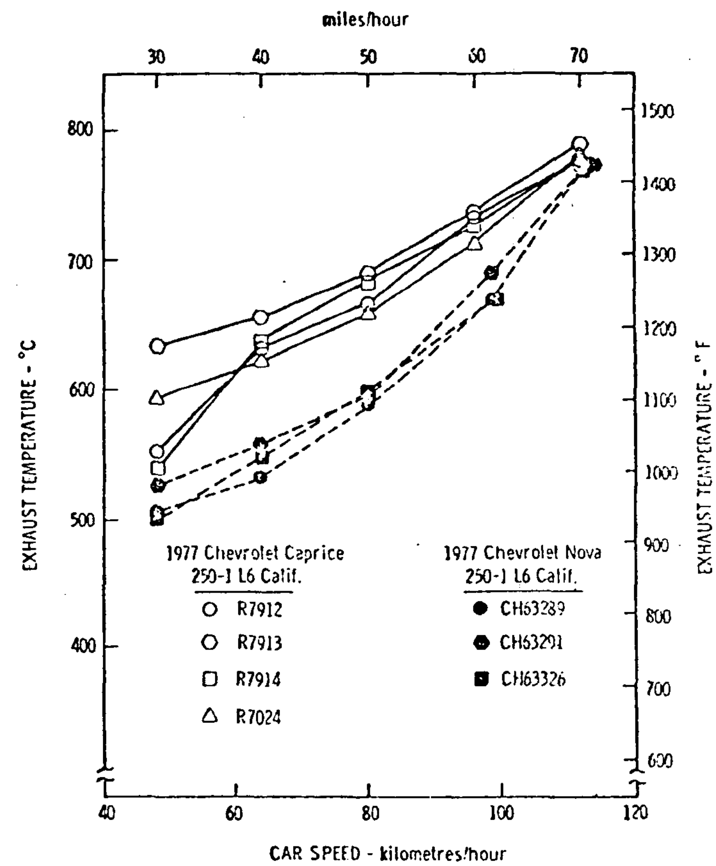


Fig. 5 - Exhaust gas temperatures at monolith inlet during road load operation

WHY DID THE BEAD-TYPE CONVERTER PLUG? - At the end of the program, the underfloor converter was removed from the Cutlass which used MMT. After the beads were removed, the converter was cut apart and photographed. A portion of the lower retainer section is shown in Figure 6. The catalyst beads and the interior of the converter housing were coated with reddish-brown deposits. Also, some of the catalyst beads were stuck in the louvers of the lower retainer. Figure 7 is a close-up view of a portion of the lower retainer. The deposits have the appearance of dry, caked mud; in some instances the deposit has nearly filled the louvers and in others, the deposit appears to have cemented the bead into the louver. Either of these situations would restrict the exhaust flow through the louvers and increase the pressure drop across the converter. These

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Table 2 - Catalyst Pressure Drop and Vehicle Acceleration Performance - Cutlasses

Car	Fuel	Test Condition	Pressure Drop Across Bead-Type Catalyst(1) kPa	(in. Hg)	Acceleration Time, sec WOT(2)	PT(3)	Engine Back Pressure (Absolute)(1) kPa	(in. Hg)
R6908	1/8 MMT	End of Test* (80 500 km)	58.6	(17.3)	14.5	-	203.6	(60.13)
	1/8 MMT	Baseline(4)	18.6	(5.5)	12.0	37.3	164.7	(48.64)
R6907	Clear	End of Test* (80 500 km)	20.7	(6.1)	11.6	29.4	166.2	(49.08)
	Clear	Baseline(4)	16.9	(5.0)	12.3	28.3	178.8	(52.80)

* Original underfloor converter, new spark plugs.

(1) Wide-open throttle, 4000 rpm.
(2) Wide-open-throttle (WOT) acceleration, 0-98 km/h (0-60 mph).
(3) Part-throttle (PT) acceleration, 56-80 km/h (35-50 mph) at 34 kPa (10 in. Hg).
(4) Baseline tests with new underfloor converter, new spark plugs.

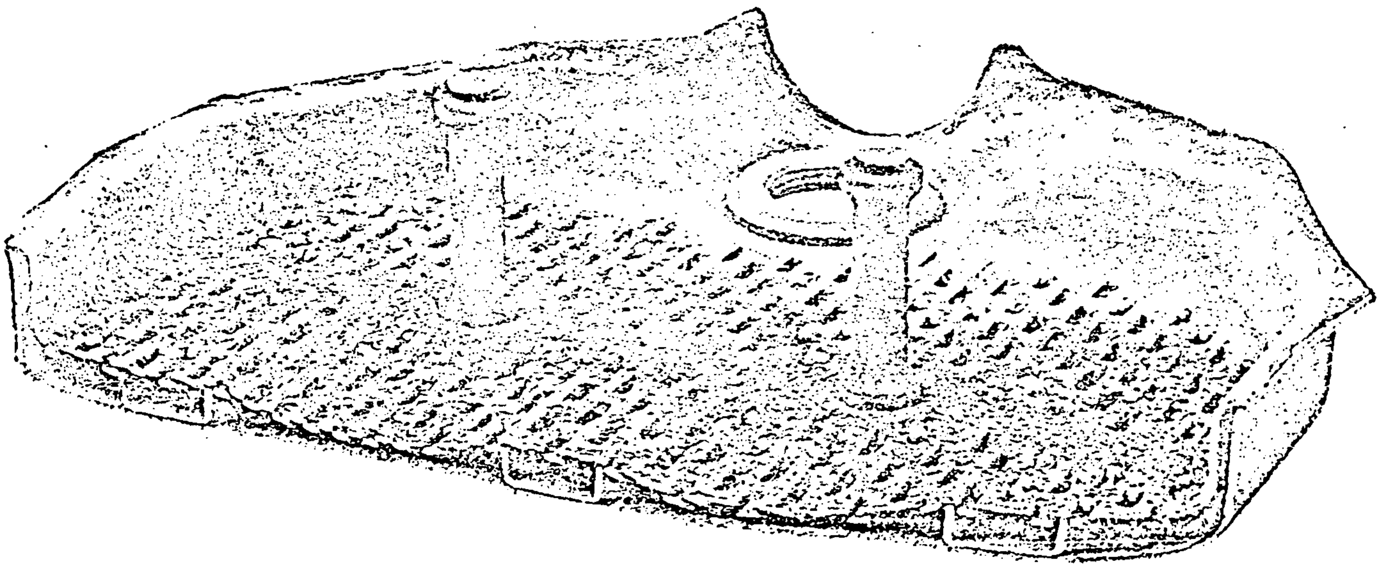

Fig. 6 - Lower retainer section of underfloor converter from R6908 Cutlass (1/8 MMT fuel)

reddish-brown deposits were analyzed and found to contain manganese oxide (Mn_3O_4), iron oxide (Fe_2O_3), and manganese iron oxide ($MnFe_2O_4$) with traces of compounds from the engine oil.

Metallographic analysis of steel components in the converter indicated that bed temperatures probably did not exceed 871 to 927°C (1600 to 1700°F) and that very little metal oxidation had occurred. No alpha alumina was found in the catalyst beads, so the converter probably was not exposed to overtemperature operation.

For comparison, the converter from the other Cutlass which used Clear Fuel was also examined. Figure 8 is a photograph of a portion of the lower retainer. Although some beads were stuck in the louvers, most louvers were not restricted by any deposit accumulation. The pressure drop across this converter increased only 3.8 kPa (1.1 in. Hg) during 80 000 km.

At the end of the test program, exhaust temperatures at the converter inlet were measured on the dynamometer during the driving schedule. Temperature distributions for both

Fig. 7 - Close-up view of lower retainer section shown in Fig. 6 (1/8 MMT fuel)

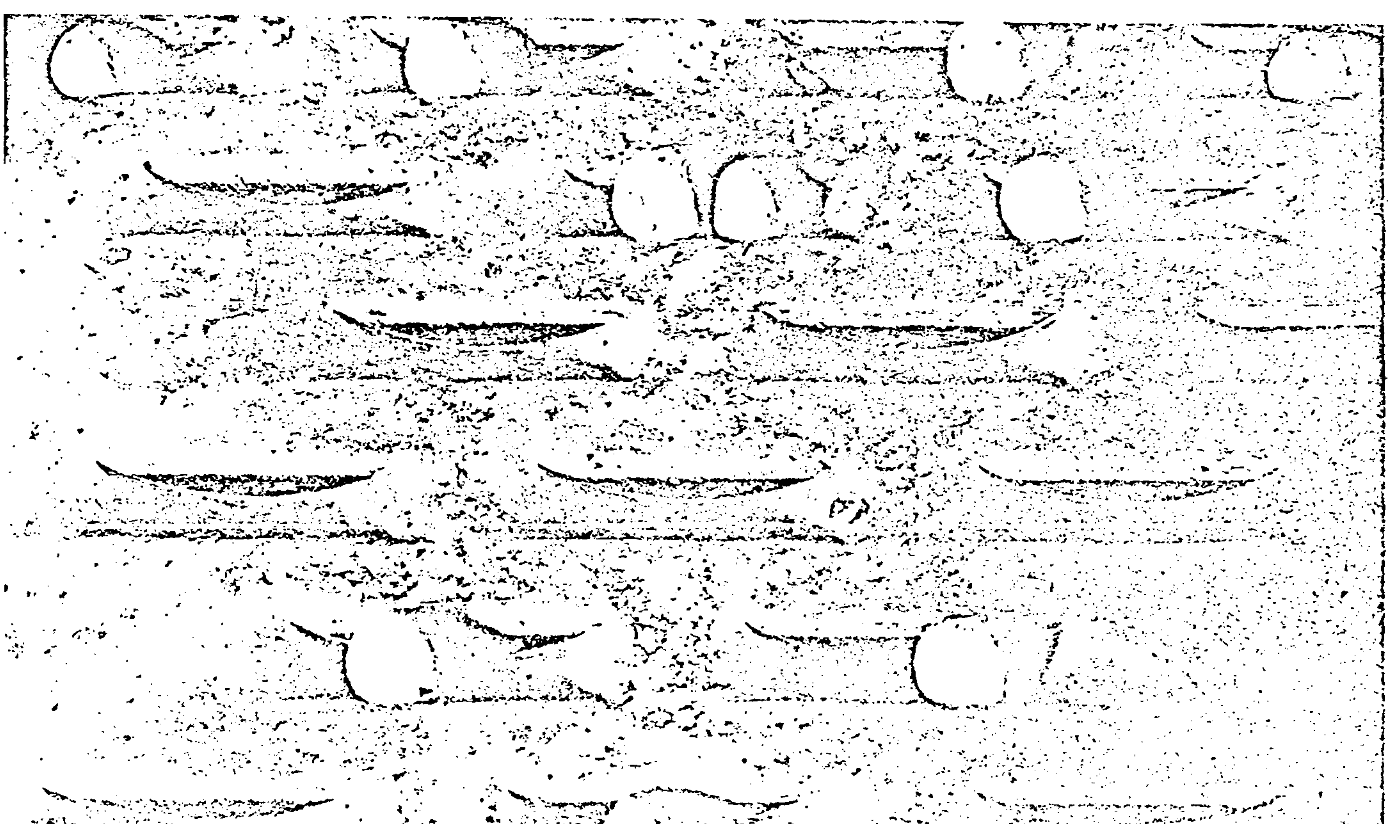

Fig. 8 - Close-up view of lower retainer section of underfloor converter from R6907

Cutlasses are plotted in Figure 9. Exhaust temperatures were similar for both cars and did not exceed 677°C (1250°F). The average temperature for both cars was about 482°C (900°F). These temperatures were substantially lower than those plotted in Figure 4 for the Novas. This was expected since the Nova temperatures were measured in the outlet of the exhaust manifold, whereas the Cutlass temperatures were measured in the exhaust pipe several feet away from the exhaust manifold. These temperature observations suggest that plugging of the underfloor converter was not caused by operation at excessively high temperature, but by deposit accumulation in the louvers as discussed previously. The mechanism of deposit accumulation in the underfloor converter is unknown.

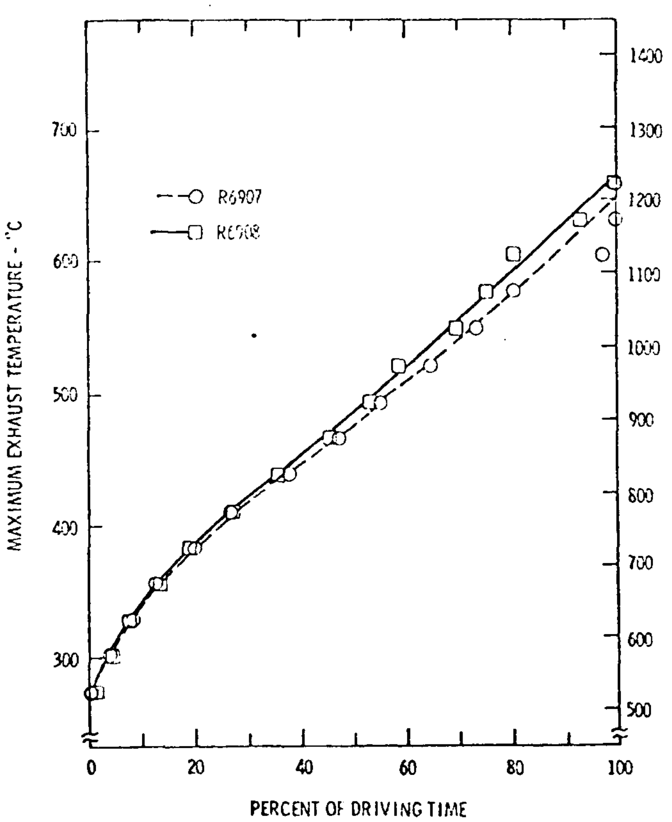

Fig. 9 - Distribution of exhaust gas temperatures at underfloor converter inlet during R007D driving schedule - Cutlasses

In addition to the converter plugging caused by MMT, exhaust emissions of the vehicles were also affected.

EXHAUST EMISSIONS

Emissions were measured simultaneously at the engine (ahead of the converter) and at the tail pipe (after the converter). This allowed determination of the catalyst's conversion efficiency. Only single emission tests were run at each mileage interval, so repeatability data are not available for these cars. At the end of the program, exhaust particulate emissions from two cars were also measured. All of these emissions results are discussed in the following sections.

EMISSIONS FROM THE ENGINE - Hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NO_x) emissions from the engine of CH63291 Nova are shown in Figure 10. These plots show that each time the monolithic converter plugged, CO emissions increased and NO_x emissions decreased. This effect was probably due to the increased engine back pressure caused by the plugged converter. As the back pressure increased, the throttle opening probably also increased to maintain appropriate vehicle speeds during the driving schedule. This would increase the amount of vehicle operation during power enrichment of the carburetor and cause richer air-fuel (A/F) ratios and higher CO emissions. Previous work (8) has shown that both increasing exhaust pressure (increasing charge dilution) and enrichening A/F ratio from stoichiometric cause a decrease in NO_x emissions which is consistent with the data shown in Figure 10. The effect of converter plugging on engine HC emissions is unclear. When the first monolith plugged, HC emissions increased, but when the next two monoliths plugged there was little effect on HC emissions.

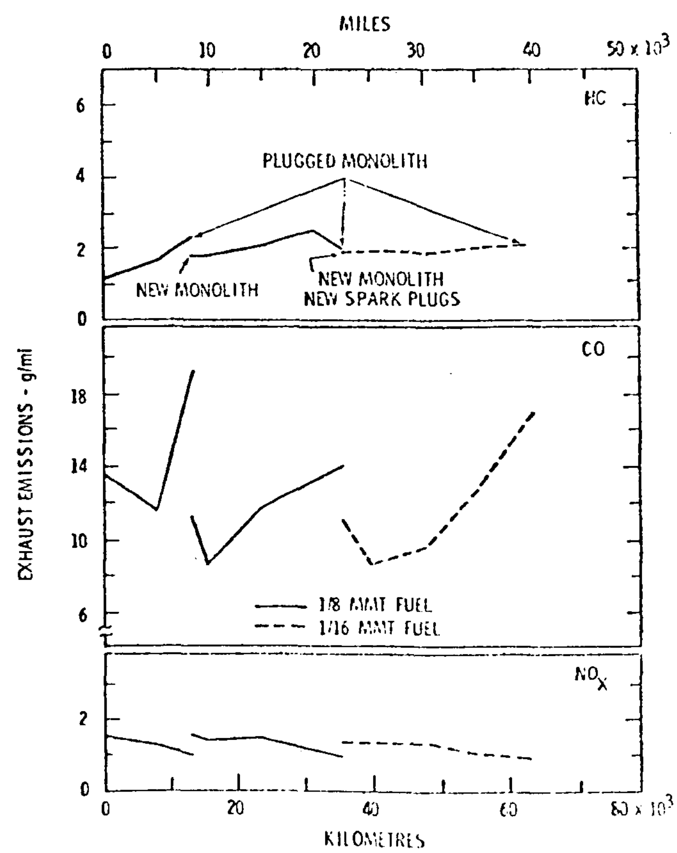

Fig. 10 - Exhaust emissions from the engine of CH63291 Nova

Similar engine emissions data are shown in Figure 11 for the other two Novas and in Figure 12 for the two Cutlasses. After 80 000 km

5 ,000 miles), HC and CO emissions were higher and NO_x emissions were lower for the cars which used 1/8 MMT Fuel compared to the companion cars which used Clear Fuel, but the differences for the Novas were quite small. There may be several reasons for this behavior. As mentioned previously, the monolith on CH63289 Nova was plugged after 80 000 km and the underfloor bead-type converter on R6908 Cutlass was partially plugged at the end of the program.

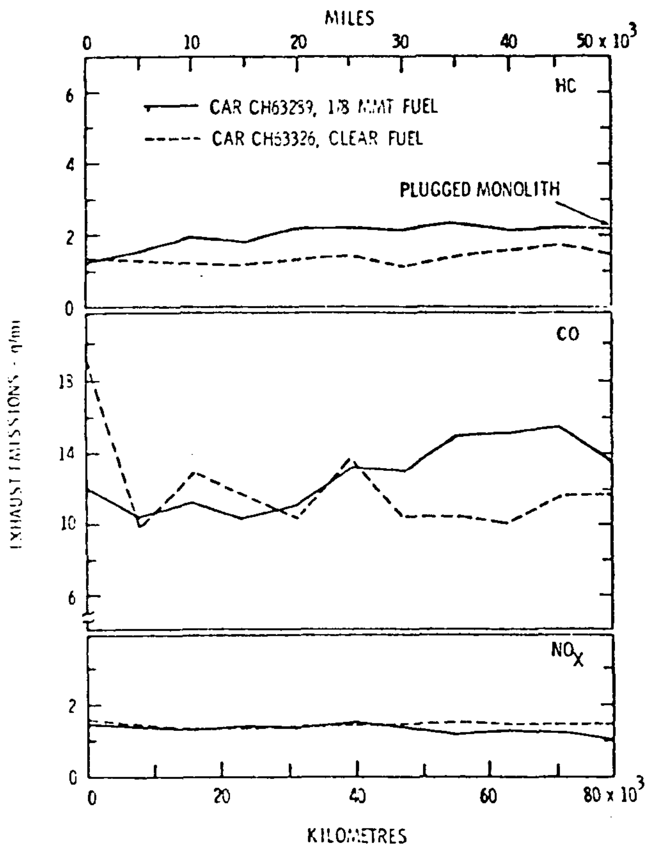

Fig. 11 - Exhaust emissions from the engines of CH63289, CH63326 Novas

Thus exhaust pressures had increased on both cars and could account for the increased CO and decreased NO_x. Most of the difference in HC emissions occurred within the first 30 000 km (20,000 miles) and then the difference remained relatively constant for the remainder of the test. Since there was little if any fuel effect on CO and NO_x during the first 30 000 km, the converters had probably not started to plug and the difference in HC was probably due to other factors.

WHY DOES MMT INCREASE ENGINE HC EMISSIONS? - To evaluate several variables which may have affected engine HC emissions, some additional tests were run on two cars at the end of the program. Results for CH63289 Nova are shown in Figure 13. After 80 000 km, engine HC had increased to 1.8 times the original level with a new engine. Spark plugs accounted for about 35 percent of the total HC increase, monolithic converter plugging about percent and combustion chamber deposits

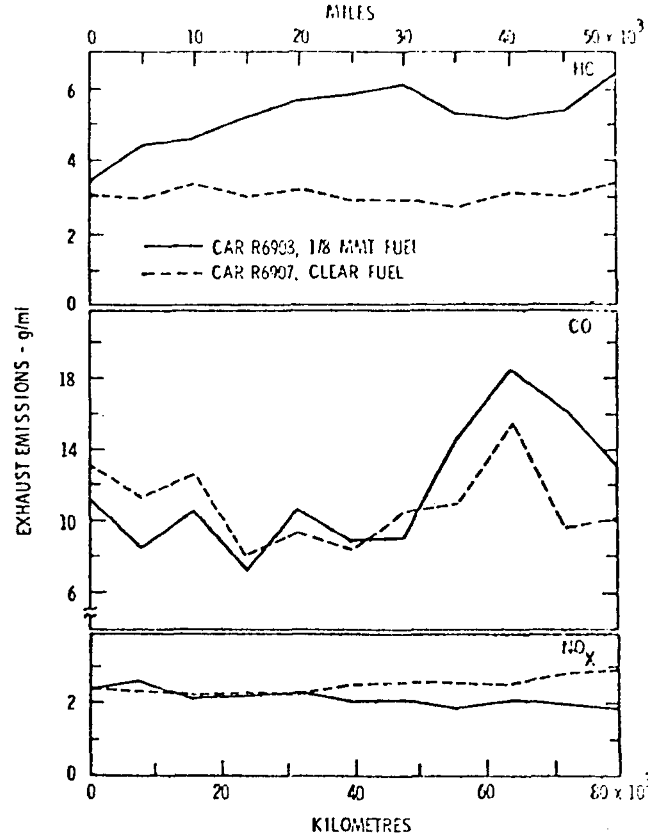

Fig. 12 - Exhaust emissions from the engines of R6907, R6908 Cutlasses

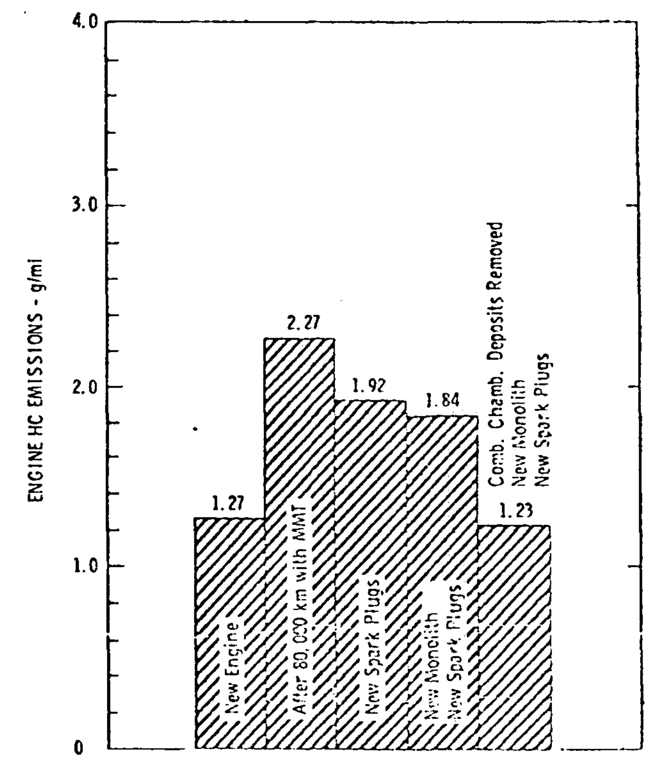

Fig. 13 - Some parameters which affected engine HC emissions - CH63289 Nova

the valves were lapped, but HC emissions were not affected. A static leak check also indicated no appreciable valve leakage prior to lapping, so apparently MMT did not affect valve

Similar tests were begun for R6908 Cutlass, but as the engine was disassembled for deposit removal it was discovered that the distributor had worn excessively; the centrifugal advance weights did not retract fully at low engine speed. Centrifugal advance curves are compared in Figure 14. It can be seen that the worn distributor gave more spark advance below 3000 rpm and less advance above 3000 rpm compared to the curve obtained with the same distributor at the beginning of the test. Distributors were also checked on all other cars in this program, but none had worn appreciably (less than about 1 degree of spark advance). Because of the distributor problem on R6908, we were unable to determine how much of the engine HC increase shown in Figure 12 was due to changes in spark advance and how much was due to combustion chamber deposits.

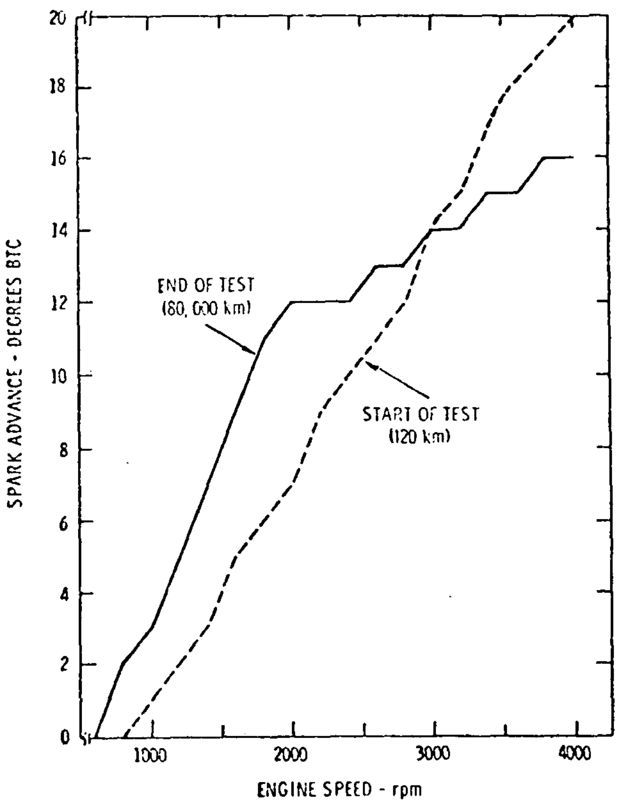

Fig. 14 - Change in centrifugal spark advance - R6908 Cutlass, 1/8 MMT fuel

It has been previously established (9) that combustion chamber deposits increase engine HC emissions. Thus, for both the Nova and the Cutlass discussed earlier, combustion chamber deposits probably contributed to the increases in engine HC emissions with MMT fuel. To determine what the underlying mechanism might be, the deposits were examined and analyzed. Figure 15 is a photograph of one of the combustion chambers of R6908 Cutlass which used 1/8 MMT Fuel. The deposits are mottled, and it appears that some of the deposits have broken away from the surface of the combustion chamber, particularly around the spark plug.

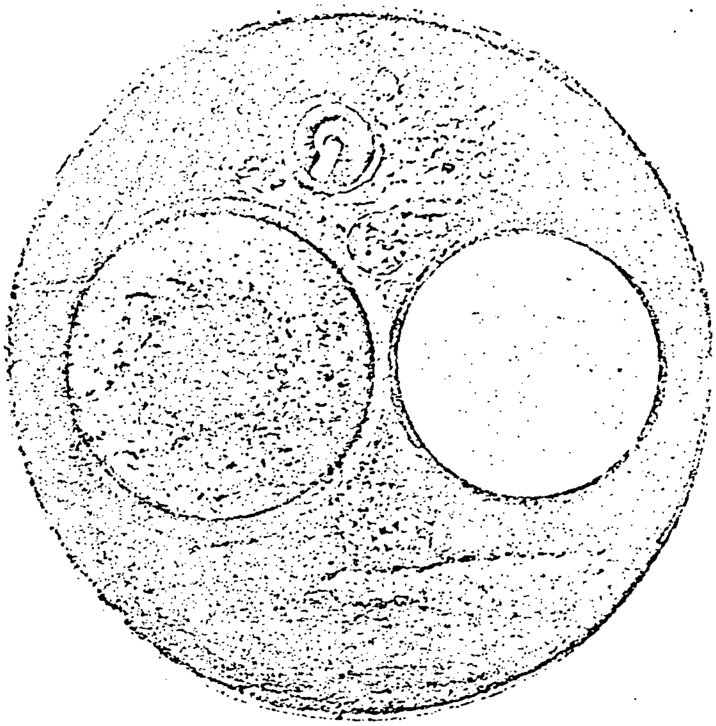

Fig. 15 - Deposits in combustion chamber of R6908 Cutlass (1/8 MMT fuel)

The area within the dotted circle was examined under a microscope and photographs were taken at 21.5 and 60.5 magnification as shown in Figure 16. Numerous voids in the deposits were evident from the microscopic examination. For comparison, deposits in the combustion chambers of R6907 Cutlass (which used Clear Fuel) were also examined, and photographs are shown in Figures 17 and 18. It appears that the deposits with Clear Fuel had fewer voids and perhaps were more uniform in some areas of the chamber compared to the 1/8 MMT Fuel deposits. This observation suggests that the MMT deposits may act like a sponge to trap pockets of unburned fuel-air mixture next to the walls. The flame may be quenched before these pockets of mixture are burned, so the voids in these deposits would be equivalent to increasing the quench layer. Daniel and Wentworth (10) have found that wall quenching is the primary source of HC emissions, and that increasing the thickness of the quench zone would be expected to increase HC emissions.

Another related explanation is that HC emissions increase because MMT deposits may have better thermal insulation properties than Clear Fuel deposits. Samples of combustion chamber deposits from CH63289 using 1/8 MMT Fuel were analyzed and the results are summarized in Table 3. The MMT fuel deposits were primarily Mn_3O_4 and carbon, and the Clear Fuel deposits (from Reference 11) were primarily carbon. Thus the two different kinds of deposits probably have different insulating properties. However, any major differences in deposit thermal properties would also be

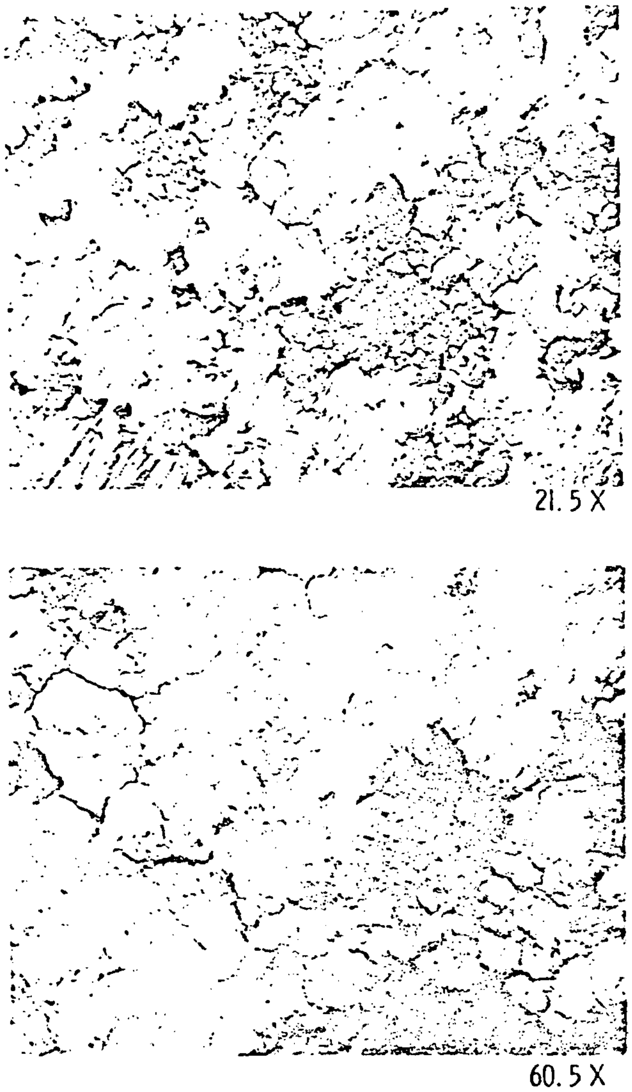

Fig. 16 - Microscopic views of deposits within dotted circle in Fig. 15

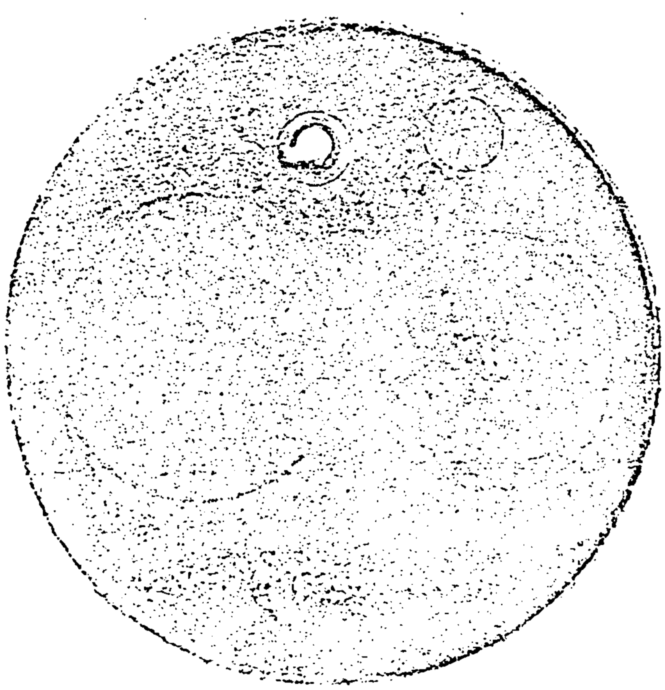

Fig. 17 - Deposits in combustion chamber of R6907 Cutlass (clear fuel)

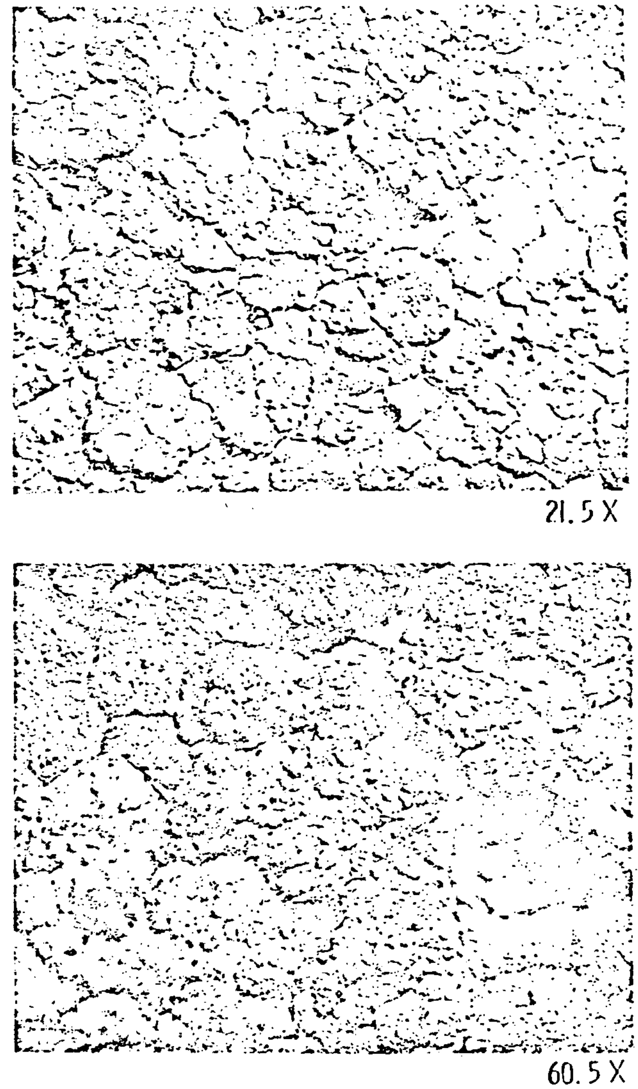

Fig. 18 - Microscopic views of deposits within dotted circle in Fig. 17

expected to affect octane requirement increase (11). But as shown in Figure 19, there was little difference in octane requirement increase with the MMT Fuel compared to Clear Fuel for the Novas. For the Cutlasses, any MMT effect is unclear because of the distributor problem discussed earlier.

In addition to exhaust emissions from the engine, emissions from the tail pipe were also analyzed since these must meet legislated exhaust emission standards.

EMISSIONS FROM THE TAIL PIPE - Tail pipe emissions of HC, CO, and NO_x from CH63291 Nova are plotted in Figure 20. Each time the monolith plugged, CO increased and NO_x decreased which is consistent with the earlier observations of engine emissions. Also, when the first and third monolith plugged, HC emissions exceeded the 1977 California standard of 0.41 g/mi.

Figures 21 and 22 are plots of tail pipe emissions for the other two Novas and for the two Cutlasses respectively. In both instances, the cars which used 1/8 MMT Fuel finished the test with higher HC, lower CO, and lower NO_x

Table 3 - Composition of Combustion Chamber Deposits

1/8 MMT Fuel			
Car	Element	Quantitative Analysis, wt %	Avg Deposit Weight, g/cyl
CH63289	Mn	25.5	2.3
Nova 1.6	C	27.5	
	Pb	2.3	
	P	2.7	
	Ca	0.1	
	Mg	1.5	
	Zn	6.6	
	Fe	1.7	

Clear Fuel (from Ref 10)			
Car	Element	Quantitative Analysis, wt %	Avg Deposit Weight, g/cyl
3VB5.7-2	Mn	Not Analyzed	2.0
Impala V8	C	38.5	
	Pb	5.0	
	P*	1.5	
	Ca*	2.5	
	Mg*	0.04	
	Zn*	0.5	
	Fe*	2.0	

X-Ray Diffraction Analysis

Major: Mn_3O_4

Minor: $3PbO \cdot H_2O$
$FePO_4$
Fe_2O_3

* Semiquantitative analysis, quantitative analysis not performed.

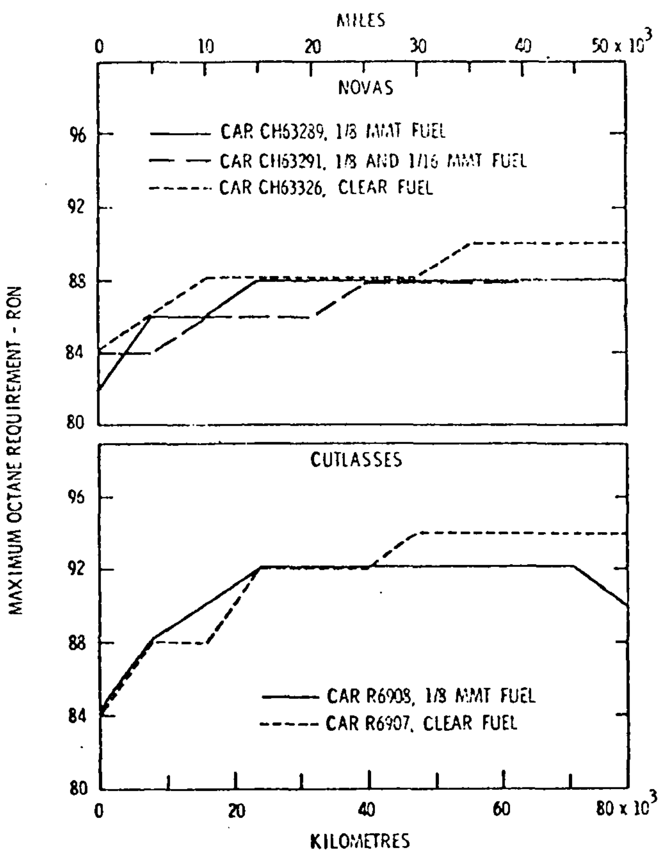

Fig. 19 - Octane requirements of Novas and Cutlasses

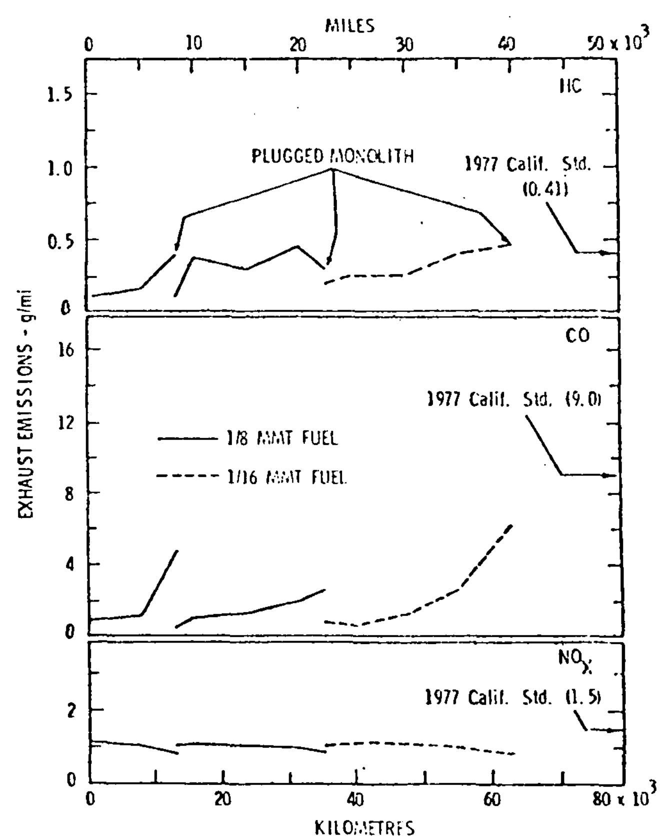

Fig. 20 - Exhaust emissions from the tailpipe of CH63291 Nova

than the corresponding cars which used Clear Fuel. However the differences were small except for the final HC data points in Figure 21. In this case the monolith on CH63289 probably plugged near the end of the program causing tail pipe HC emissions to increase sharply and exceed the 0.41 g/mi standard. All other cars met their respective emission standards for 80 000 km even though the driving schedule was different from the one normally used for emission certification.

12 are compared to tail pipe emissions in Figures 21 and 22, it appears that the catalytic converters were more active on the cars which used 1/8 MMT Fuel compared to those which used Clear Fuel. Therefore, HC and CO conversion efficiencies were also examined for these cars.

CONVERSION EFFICIENCIES - Figures 23 and 24 show HC and CO conversion efficiencies, respectively, for the two Novas which accumulated 80 000 km. These efficiencies and those

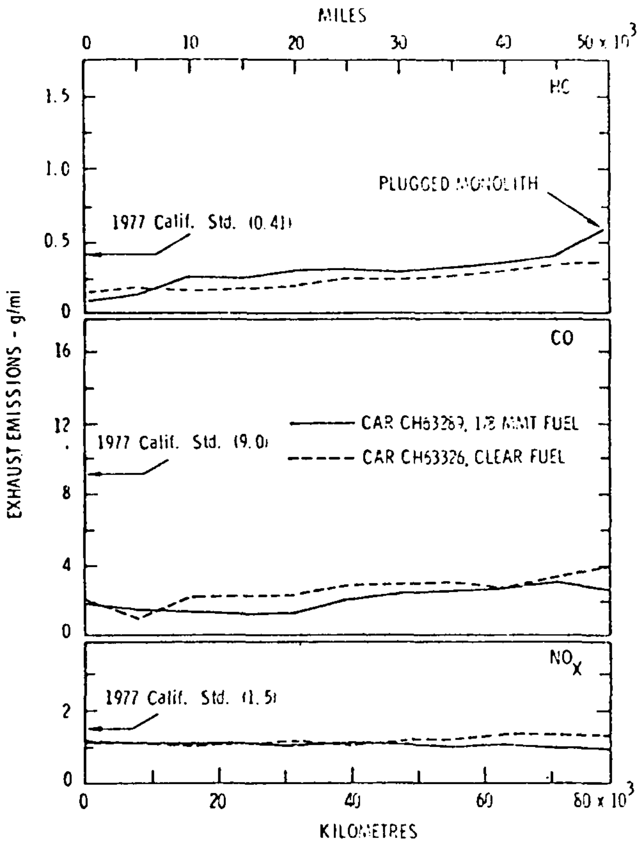

Fig. 21 - Exhaust emissions from the tailpipes of CH63289, CH63326 Novas

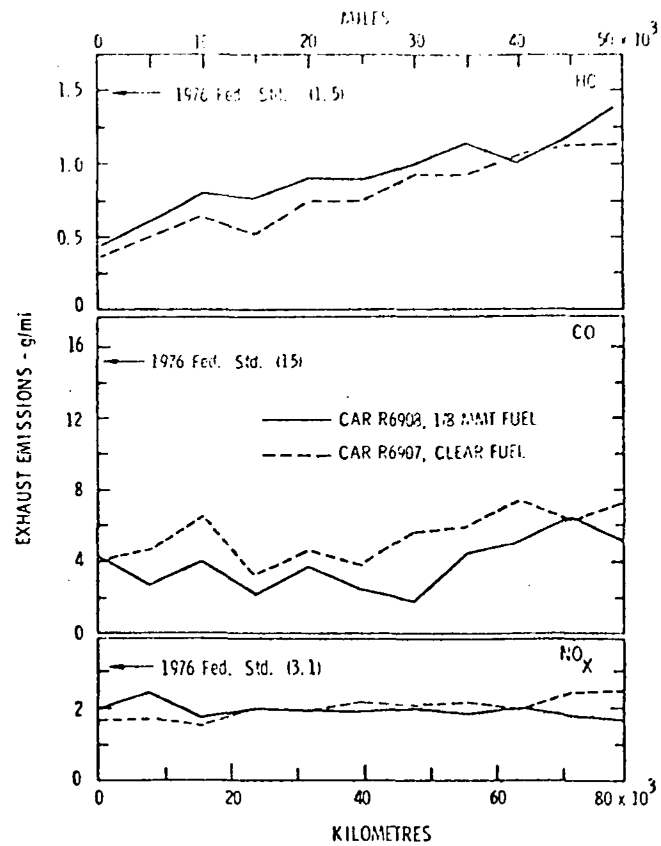

Fig. 22 - Exhaust emissions from the tailpipes of R6907, R6908 Cutlasses

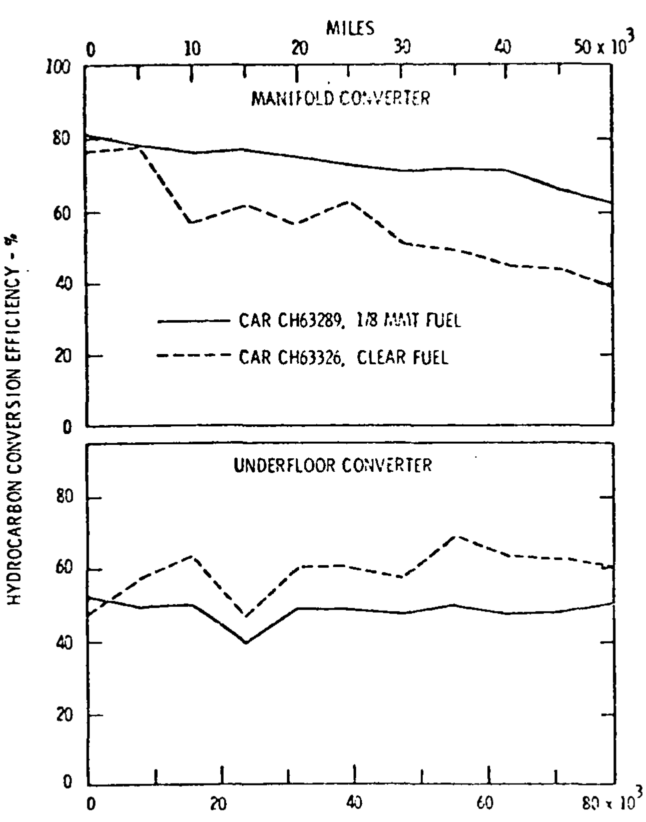

Fig. 23 - Hydrocarbon conversion efficiencies for CH63289, CH63326 Novas

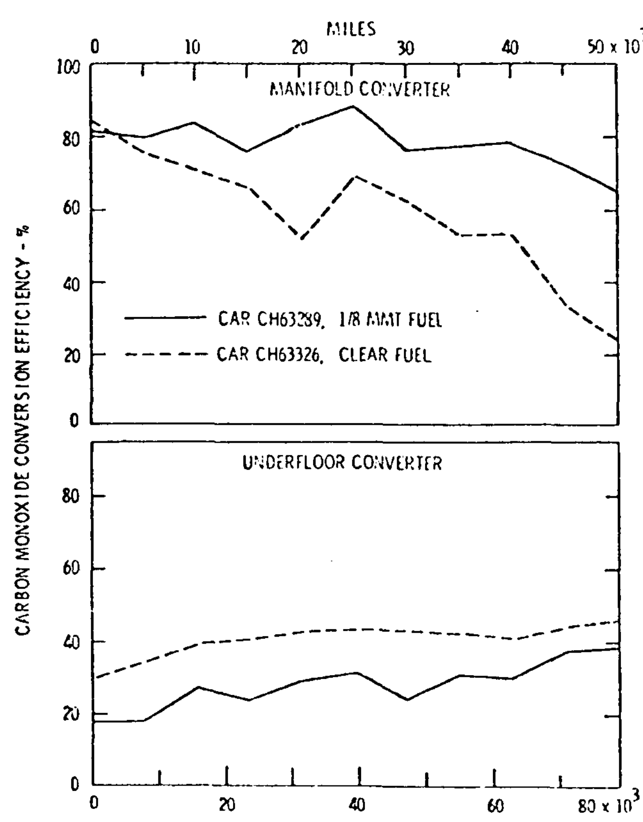

Fig. 24 - Carbon monoxide conversion efficiencies for CH63289, CH63326 Novas

tail pipe emissions measured during the emission tests. Underfloor converter efficiencies were quite low because the manifold converter oxidized much of the HC and CO before the exhaust gases reached the underfloor converter. From these curves it appears that both HC and CO efficiencies for the manifold converter deteriorated less rapidly with 1/8 MMT Fuel than with Clear Fuel. There was essentially no fuel-related difference in either HC or CO deterioration rates for the underfloor converters.

Conversion efficiencies for the Cutlasses with underfloor converters are plotted in Figure 25. In this case it appears that both HC and CO efficiencies deteriorated less rapidly with 1/8 MMT Fuel than with Clear Fuel. Faggan, et al. (3), also observed higher conversion efficiencies with MMT fuel than with Clear Fuel and speculated that the manganese oxide deposits on the catalyst help promote oxidation. The lack of effect on the underfloor converters of the Novas may be related to the amount of manganese oxide which reached the underfloor converter. With the Cutlasses, all of the manganese oxide in the exhaust (except that which was absorbed in the engine oil or deposited in the engine and exhaust pipes) reached the underfloor converter. With the Nova, however, the manifold converter probably trapped much of the manganese oxide before the exhaust entered the underfloor converter, thus minimizing or eliminating any beneficial effects of MMT on converter oxidation.

The conversion efficiencies observed during vehicle tests may have been influenced by the change in engine emissions, particularly HC, throughout the 80 000 km program. Another measure of the effect of MMT on underfloor converter performance was obtained from laboratory tests (12) using an exhaust feedstream of constant HC and CO composition. Results from the AC Test Cell 102 tests are summarized in Table 4. Data for the change in performance with mileage (the "delta" values) shown in Table 4 indicate that the converters which were exposed to 1/16 or 1/8 MMT Fuels suffered less performance degradation than their counterparts which were exposed to Clear Fuel. This observation was true during both warm-up and fully warmed-up operation. These laboratory results agree with the vehicle test results described previously for the Cutlasses, but disagree with those for the Novas. The laboratory tests with constant exhaust feedstream are probably more accurate than vehicle tests for evaluating converter activity because vehicle test variability has been eliminated. Therefore, it appears that MMT may have a beneficial effect on underfloor converter oxidation performance.

In addition to exhaust emissions of HC, CO, and NO_x, particulate emissions from the two Cutlasses were also measured to determine if MMT had any effect.

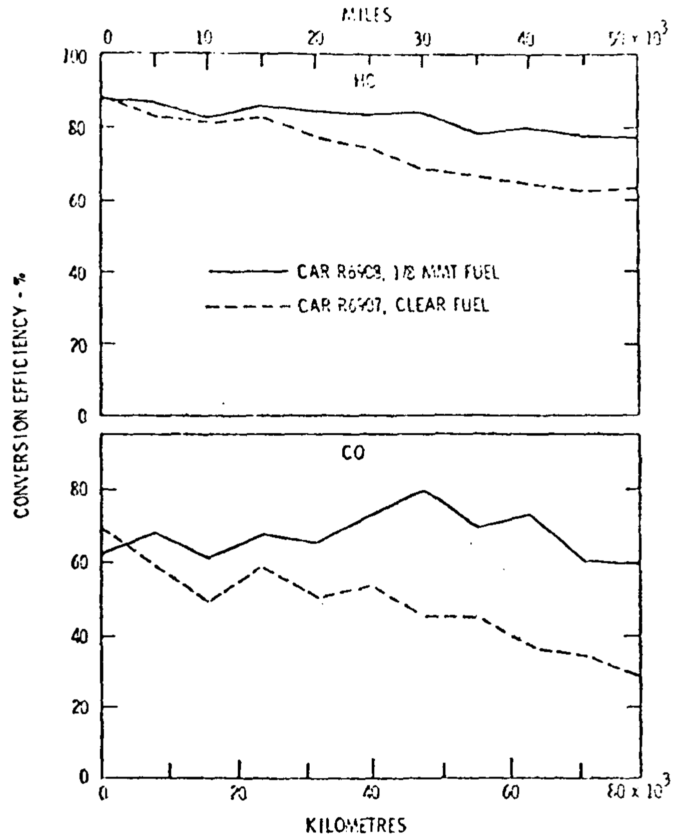

Fig. 25 - Conversion efficiencies for underfloor converters of R6907, R6903 Cutlasses

PARTICULATE EMISSIONS - Manganese emissions, sulfate emissions, and total particulate emissions were measured during the following test cycles: 1972 Federal Test Procedure (FTP) (13), Sulfate Emissions Test Cycle No. 7 (S-7) (14), Highway Fuel Economy Cycle (15), and constant speed road-load cruises at 64 km/h (40 mph) and 97 km/h (60 mph). The test procedures and equipment as well as the analytical techniques have been described by Begeman, et al. (16). Each car was tested several times on each test cycle, and the average emissions for each cycle are summarized in Table 5.

For the car which used MMT fuels, the overall average manganese emissions for all test cycles was 2.6 mg Mn/mi. At this emission rate, 29 percent of the manganese supplied in the fuel was recovered from the exhaust stream. The remaining 71 percent must have been absorbed in the engine oil and deposited in the engine, exhaust system, and catalytic converter. Both sulfate and total particulate emissions were somewhat higher for the car which used MMT fuel compared to the other car which used clear fuel. However, both cars had lower emissions than similar cars which have been reported in the literature (3,16) and are also listed in Table 5. Since sulfate and total particulate emissions from the two Cutlasses were very low, any MMT effect on particulates may be negligible in terms of ambient air quality.

Table 4 - Performance of Underfloor Converters
During AC Test Cell 102 Tests

Car	Make	Fuel	Test Condition(1)	Warm-Up Time, sec(2) HC	Warm-Up Time, sec(2) CO	Hot Efficiency, %(3) HC	Hot Efficiency, %(3) CO	Predicted Efficiency, %(4) HC	Predicted Efficiency, %(4) CO
R6908	Cutlass	1/8 MMT	I	62	51	91.9	98.7	87	80
			E	118	78	82.5	98.2	78	77
			Δ	+56	+27	-9.4	-0.5	-9	-3
R6907	Cutlass	Clear	I	61	50	92.0	99.7	87	81
			E	166	109	65.7	86.5	68	68
			Δ	+105	+59	-27.3	-13.2	-19	-13
CH63289	Nova	1/8 MMT	I	62	52	93.8	99.1	88	80
			E	103	83	87.4	99.6	82	77
			Δ	+41	+31	-6.4	+0.5	-6	-3
CH63291	Nova	1/8, 1/16 MMT	I	61	49	94.1	99.1	88	81
			E	95	79	86.7	99.8	82	78
			Δ	+34	+30	-7.4	+0.7	-6	-3
CH63326	Nova	Clear	I	60	40	94.9	99.7	89	82
			E	118	84	82.3	98.3	78	76
			Δ	+58	+44	-12.6	-1.4	-11	-6

(1) I = Initial, before mileage accumulation.
E = End of test (64 000 km for CH63291, 80 000 km for all others).
Δ = Change, E-I.
(2) Warm-up time required for converter to achieve 50% efficiency.
(3) Conversion efficiency after 600 sec of operation, converter fully warmed-up.
(4) Conversion efficiency during FTP predicted from Test Cell 102 performance.

Table 5 - Exhaust Particulate Emissions

Car	Fuel	Test Cycle	Manganese Emissions mg Mn/mi	Manganese Emissions mg Mn_3O_4/mi	Manganese Emissions % Fuel Mn Recovered	Sulfate Emissions mg H_2SO_4/mi	Sulfate Emissions % Fuel S Recovered	Total Particulate Emissions mg/mi	Total Particulate Emissions % Mn_3O_4	Total Particulate Emissions % H_2SO_4	No. of Tests
R6908 Cutlass	1/8 MMT	1972 FTP - Cold Start	6.3	8.8	59.2	0.54	1.5	23.7	36.1	2.2	4
	0.005% S	- Hot Start	3.6	5.0	38.3	0.37	1.2	15.5	33.7	2.6	7
		S-7	1.9	2.4	23.1	0.84	3.0	9.3	29.0	9.7	6
		Highway Fuel Economy	1.6	2.1	22.0	0.78	3.1	11.3	20.6	9.1	6
		40 mph Cruise	1.0	1.4	16.5	0.36	1.7	4.9	31.0	9.2	6
		60 mph Cruise	1.2	1.4	15.1	1.50	5.5	4.7	34.8	32.3	6
		Overall Avg	2.6	3.5	29.0	0.73	2.7	11.6	30.9	10.9	
R6907 Cutlass	Clear	1972 FTP - Cold Start				0.17	0.5	6.7		2.5	5
	0.005% S	- Hot Start				0.09	0.3	6.2		1.4	7
		S-7				0.07	0.3	5.3		1.5	6
		Highway Fuel Economy				0.20	0.9	4.6		5.1	6
		40 mph Cruise				0.12	0.6	1.8		7.0	6
		60 mph Cruise				0.89	3.9	3.2		28.0	6
		Overall Avg				0.26	1.1	4.6		7.6	
Ethyl Data: (Ref 3)											
1971 Noncatalyst	1/8 MMT	Unknown						97			
	Clear							81			
GMR Data: (Ref 16)											
Noncatalyst, One Car	Clear, 0.03% S	1972 FTP - Cold Start				1.0	0.3	26			
Pellet-Type Catalyst, Four-Car Avg	Clear, 0.03% S	1972 FTP - Cold Start				1.8	0.8	29			

FUEL ECONOMY

During each exhaust emission test, fuel economy was computed by the carbon balance method as specified by EPA (17). The resulting values, representing city driving, are plotted in Figure 26 for the four cars which accumulated 80 000 km, and in Figure 27 for the Nova which repeatedly plugged monolithic converters. Figure 26 shows that after 80 000 km both cars which used MMT fuel had about 1 mile per gallon (mpg) poorer fuel economy than their counterparts which used clear fuel. As mentioned earlier, the monolith on CH63289 was plugged, and the underfloor converter on R6908 was partially plugged after 80 000 km. In addition R6908 had a distributor wear problem. Figure 27 shows that each time a monolith plugged, fuel economy also dropped. As the converters plugged, engine back pressure increased which would be expected to decrease fuel economy via reduced volumetric efficiency and increased throttle openings (carburetor enrichment). To determine more precisely the effect of back pressure on fuel economy, some additional tests were run with two cars.

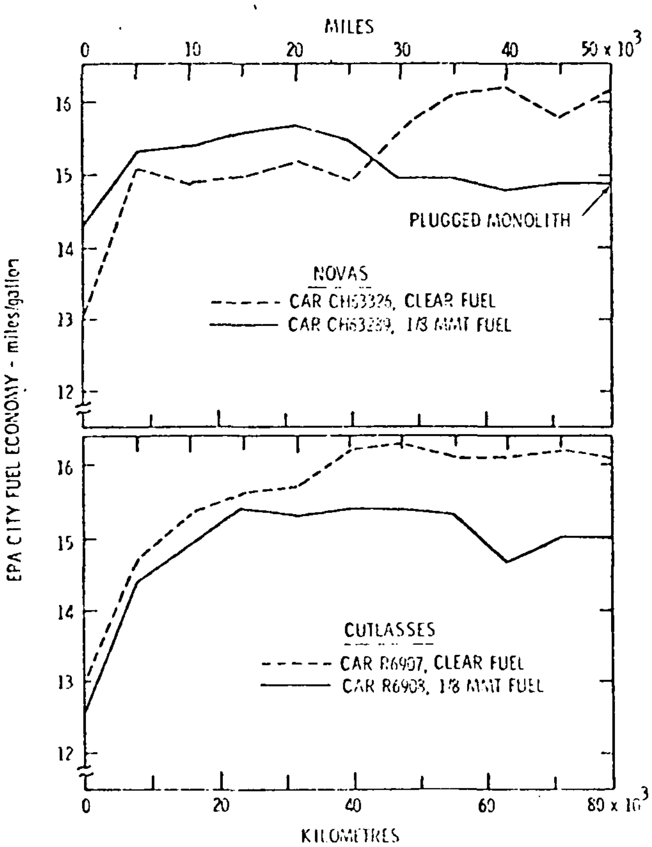

Fig. 26 - Fuel economy for Novas and Cutlasses throughout 80 000 km

After 80 000 km, engine deposits were removed, new spark plugs were installed and new catalytic converters were installed on R6908 Cutlass and CH63289 Nova. A new distributor was also installed in R6908. Then multiple tests were run on each car, first in the non-

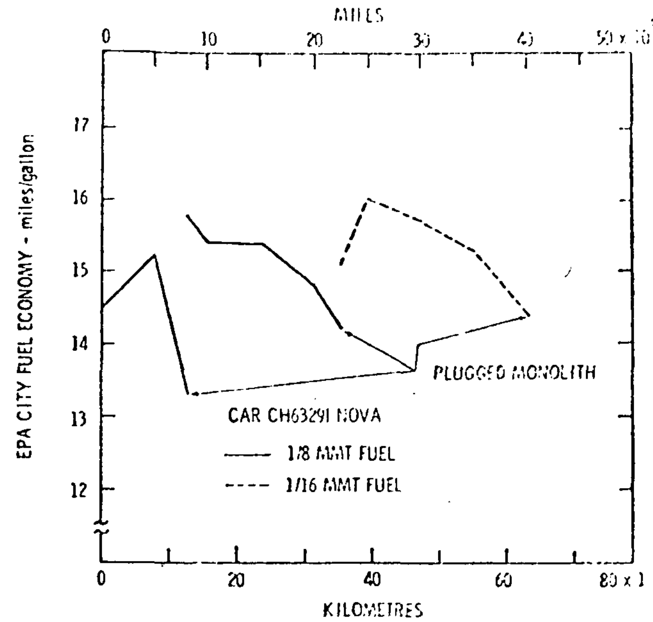

Fig. 27 - Fuel economy for Nova which repeated plugged monolithic converters

striction which provided about the same engine back pressure experienced by each car after 80 000 km (listed in Tables 1 and 2). Fuel economy data are summarized in Table 6. For each car, the city, highway, and composite fuel economies decreased as engine back pressure increased. However, in most cases the reductions in fuel economy were small, from 1.5 to 3.5 percent for the Nova and from 0.5 to 1.5 percent for the Cutlass, and may even be within the range of test repeatability. The smaller loss with the Cutlass may have been due to a higher power-to-weight ratio and therefore less frequent carburetor power enrichment during the driving cycles compared to the Nova. It should be noted that the most severe case of monolith plugging (monolith No. 1 on car CH63291) was not simulated, but had it been, fuel economy would probably have been reduced more than 1.5 to 3.5 percent.

It should also be noted that the reduced fuel economy due to converter plugging with MMT fuels would only apply when the converter is plugging or plugged. The plugging is obviously a gradual process, and thus the fuel economy losses would also occur gradually.

An additional fuel economy penalty may be incurred if initial engine calibrations have to be changed to compensate for increased engine HC emissions with MMT. One of the most effective methods of reducing HC from the engine is to retard spark timing, but this also reduces fuel economy. The magnitude of these reductions is probably different for each engine design, but it is possible that some engine families may have difficulty meeting future emission standards or future fuel economy standards if MMT is used in the fuel. More experimental work is needed to quantify these

Table 6 - Effect of Engine Back Pressure on Fuel Economy

Car	Exhaust Restriction	Engine Back Pressure (Absolute)(1) kPa	(in. Hg)	EPA City Economy, mpg	EPA Hwy Economy, mpg	EPA Composite 55/45 Economy, mpg
CH63289 Nova	None	156.4	(46.2)	14.4	20.6	16.7
	End of Test(2)	170.0	(50.2)	13.9	20.3	16.2
	% Change	+8.7	(+8.7)	-3.5	-1.5	-3.0
R6908 Cutlass	None	164.7	(48.6)	13.6	18.4	15.4
	End of Test(3)	202.1	(59.7)	13.4	18.3	15.3
	% Change	+22.8	(+22.8)	-1.5	-0.5	-0.6

(1) WOT, 4000 rpm.
(2) Restriction simulating plugged monolith at 80 000 km.
(3) Restriction simulating partially plugged underfloor beaded converter at 80 000 km.

SPARK PLUG DEPOSITS

As mentioned earlier, spark plugs were not changed at recommended intervals (except for CH63291) but remained in the engines for 80 000 km. Whenever spark plugs were removed from any of the cars after mileage accumulation with either 1/16 or 1/8 MMT Fuel, the electrodes and insulator tips were covered with reddish-brown deposits. Some typical examples are shown in Figure 28 for the Nova plugs and in Figure 29 for the Cutlass plugs. In some

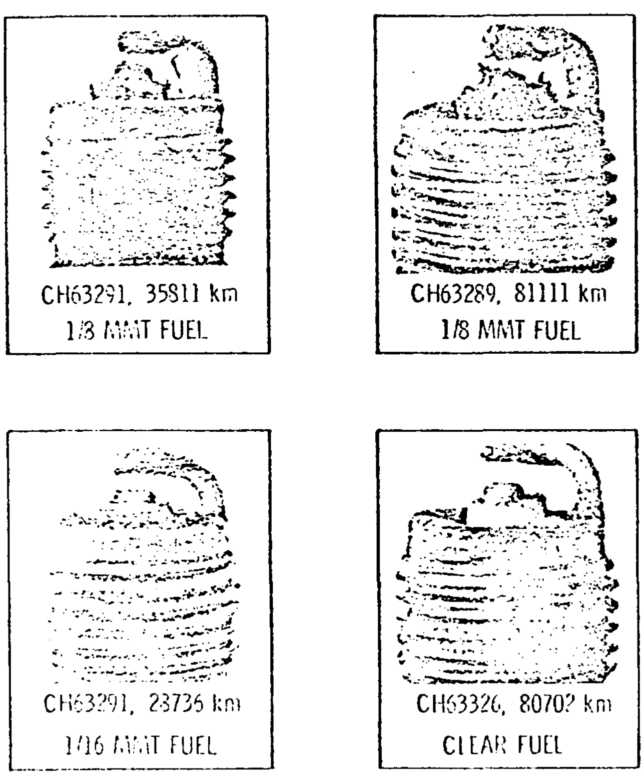

Fig. 28 - Spark plug deposits - Novas

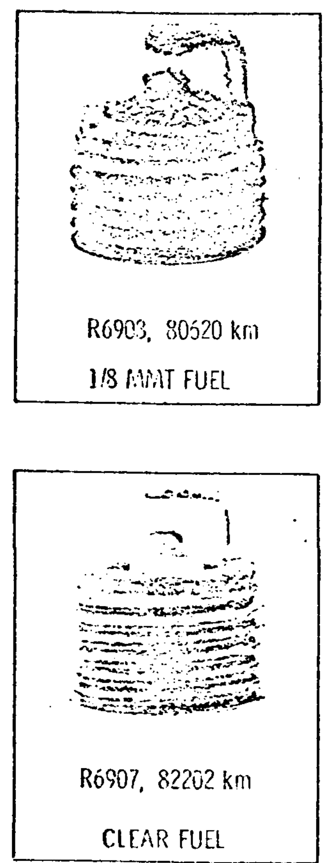

Fig. 29 - Spark plug deposits - Cutlasses

cases, deposits nearly bridged the electrode gap on the Nova plugs; these plugs had an initial gap of 0.89 mm (0.035 in.). The Cutlass plugs had a wider initial gap, 2.03 mm (0.080 in.), and were not bridged with deposits. Samples of the reddish-brown deposits

To determine whether these deposits affected spark plug performance, several exhaust emission tests, vehicle performance tests, and hot shunt resistance tests were run with each set of spark plugs. Results are summarized in Table 7. For the Cutlasses, a slight misfire was observed with R6908 (1/8 MMT Fuel) after 80 000 km, however, it was judged to be undetectable by an untrained driver. Two of the spark plugs had a hot shunt resistance of 1.4 megohms which is very close to the threshold fouling resistance of 1.0 megohm. All other plugs had much higher resistances and

For both the Cutlasses and the Novas, the effect of spark plug deposits on engine HC emissions is unclear. In some instances, HC decreased and in others, HC increased when new spark plugs were installed.

It appears that the substantial spark plug deposits with MMT fuel at the 0.034 g Mn/ℓ level probably increased tail pipe HC emissions in all three cars which used 1/8 MMT Fuel and may have caused a borderline misfire in one car. However, if plugs had been changed at the recommended interval, the misfire would probably not have occurred on R6908.

Table 7 - Spark Plug Performance

	1976 Cutlasses		1977 Novas			
	R6908	R6907	CH63291	CH63291*	CH63289*	CH63326
Deposit Accumulation Distance - km	80 620	82 202	35 811	28 736	81 111	80 702
(mi)	(50,095)	(51,078)	(22,252)	(17,856)	(50,400)	(50,146)
Manufacturer's Recommended Interval for Changing Spark Plugs - km	36 210	36 210	36 210	36 210	36 210	36 210
(mi)	(22,500)	(22,500)	(22,500)	(22,500)	(22,500)	(22,500)
Fuel Used for Deposit Accumulation	1/8 MMT	Clear	1/8 MMT	1/16 MMT	1/8 MMT	Clear
Engine HC Emissions:						
Before Plug Change, g/mi	7.01	3.18	2.18	2.13	2.27	1.55
After Plug Change, g/mi	6.48	3.47	1.92	2.48	1.92	1.65
Change in Emissions, g/mi	-0.53	+0.29	-0.26	+0.35	-0.35	+0.10
Tail Pipe HC Emissions:						
Before Plug Change, g/mi	0.74	0.44	0.33	0.47	0.60	0.18
After Plug Change, g/mi	0.63	0.46	0.19	0.52	0.28	0.17
Change in Emissions, g/mi	-0.11	+0.02	-0.14	+0.05	-0.32	-0.01
WOT Acceleration, 0-96 km/h (0-60 mph):						
Before Plug Change, sec	13.8	12.6	-	28.5	23.9	21.6
After Plug Change, sec	12.0	12.3	-	25.6	22.5	22.9
Change in Accel Time, sec	-1.8	-0.3	-	-2.9	-1.4	+1.3
Spark Plug Hot Shunt Tests:						
No. of Plugs Fouled	2 (borderline)	0	0	0	0	0
Misfire Observations	Trace**	None	None	None	None	None

* Tests with plugged monolith, all other tests with Novas with new monoliths, all tests with Cutlasses with new underfloor converters.
** Misfire at idle and from 0-40 mph WOT.

were not fouled. New spark plugs decreased tail pipe HC emissions about 15 percent and decreased WOT acceleration time 1.8 sec for car R6908 which used MMT fuel. By contrast, new spark plugs did not appreciably affect tail pipe HC emissions or acceleration performance of car R6907 which used Clear Fuel.

For the Novas, no misfire was observed and none of the plugs were fouled; all had hot shunt resistances greater than 3 megohms. When new spark plugs were installed, tail pipe HC emissions decreased 40 percent for CH63291 (1/8 MMT Fuel) and 50 percent for CH63289 (1/8 MMT Fuel), but did not change appreciably for CH63291 (1/16 MMT Fuel) and CH63326 (Clear Fuel). The effect of new spark plugs on WOT acceleration times may not be significant since both increases and decreases were observed.

SHOULD MMT BE USED IN UNLEADED FUELS OF THE FUTURE?

The energy benefits of using MMT to increase antiknock quality and refinery yield have been estimated to be about 1 percent savings in terms of total crude oil usage (18). However, our limited vehicle test work has shown that under certain driving conditions, MMT may plug catalytic converters and may also increase HC emissions. As discussed previously, both of these problems could cause fuel economy penalties. First, converter plugging increases engine back pressure and consequently, fuel consumption also increases, although our data indicate that the increase is quite small. Secondly, if crease to the point where vehicles will not meet future more restrictive emission standards, new engines will have to be recalibrated, and as a result, fuel consumption will probably increase. These penalties in vehicle fuel economy could conceivably negate the benefits of using MMT at the refinery, and an overall energy loss might occur.

At this point several questions remain. Obviously, more experimental work is needed before an overall energy assessment can be made to decide whether MMT should be used in unleaded gasolines of the future. Additional work is also needed to determine whether catalyst plugging would be a serious field problem and whether increases in HC emissions threaten to negate emissions control gains made to date. Because of these uncertainties, it seems prudent to limit the usage and concentration of MMT until some of the potential vehicle compatibility problems can be resolved.

SUMMARY

Two 1976 Cutlasses with Federal emission control systems (underfloor bead-type converters) and three 1977 Novas with California emission controls (close-coupled monolith and underfloor bead-type converters) were tested for 80 000 km (50,000 miles) on chassis dynamometers. The driving schedule included 113 km/h (70 mph) steady speeds and was somewhat more severe than the emission certification schedule. Based on experimental results from these five vehicles, it appears that continuous use of MMT fuel additive at a concentration of 0.034 g Mn/ℓ (0.129 g Mn/gal) can cause vehicle problems.

Several close-coupled monolithic converters plugged after operation varying from 14 000 to 80 000 km (8500 to 50,000 miles), and one underfloor bead-type converter partially plugged during the 80 000 km (50,000 mile) test. With close-coupled monoliths, plugging caused driveability complaints and reduced acceleration performance. The partially-plugged underfloor converter did not cause any driver complaints. However, with both types of converters, fuel economy decreased from 0.5 to 3.5 percent as the converters plugged.

Engine hydrocarbon emissions increased from 85 to 190 percent for the three vehicles which used MMT fuel. This increase was partially offset by an apparent benefit of MMT on catalytic converter efficiency; converter activity deteriorated less rapidly with MMT fuel compared to clear fuel. However, if initial engine calibrations must be changed to compensate for increased hydrocarbon emission caused by MMT, fuel consumption will probably increase and meeting future emission and fuel economy standards will be more difficult.

Particulate emissions were somewhat higher for the Cutlass which used MMT fuel compared to the Cutlass which used clear fuel. However, both cars had very low total particulate emissions. Only 29 percent of the manganese supplied in the fuel was recovered in the exhaust. The other 71 percent must have been absorbed in the engine oil and deposited in the engine, exhaust system, and catalytic converter.

Excessive spark plug deposits were observed whenever MMT fuel was used. If the spark plug change interval is extended to 80 000 km, these deposits may cause a deterioration in performance and may result in increased hydrocarbon emissions and misfire. However, if the manufacturer's recommended intervals are observed, these effects probably will not be observed.

The use of MMT did not affect the rate at which octane requirements increased.

CONCLUSION

The use of MMT can deteriorate exhaust emission control systems and cause driveability complaints if vehicles operate under rigorous driving conditions. In addition, use of MMT may decrease vehicle fuel economy to a certain extent. More experimental work is needed before an overall assessment can be made to either justify continuing or expanding the use of MMT, or to ban it from unleaded gasolines.

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Appendix A

TEST EQUIPMENT AND EXPERIMENTAL PROGRAM

FUELS AND OIL - The unleaded gasoline which is normally used for mileage accumulation during exhaust emission certification tests was the base gasoline for this program, and will be designated "Clear Fuel." Two additional batches of fuel were prepared by adding MMT to the base gasoline at concentrations of 0.034 g Mn/ℓ (0.129 g Mn/gal) and 0.017 g Mn/ℓ (0.064 g Mn/gal); these fuels will be designated "1/8 MMT Fuel" and "1/16 MMT Fuel" respectively. Inspection data for all three fuels are shown in Table 1A.

A 10W-30 engine oil was used in all five cars. Engine oil and oil filters were changed at manufacturer's recommended service intervals (12 000 km for oil, 12 000 km and every 24 000 km thereafter for filter).

CARS - Five cars were tested: two 1976 Oldsmobile Cutlasses with Federal exhaust emission controls and three 1977 Chevrolet Novas with California emission controls. Specifications and equipment for each car model are summarized in Table 2A. One of the major differences between these two car models was the catalytic converter system. The Cutlasses used a conventional underfloor bead-type catalyst, and the Novas used a monolithic catalyst closely coupled to the exhaust manifold in addition to the underfloor bead-type catalyst. A schematic of the close-coupled monolith is shown in Figure 1A. Note that this converter contains two sections of monolith in series separated by a 1.5 mm (0.060 in.) gap. The purpose of this manifold converter is to provide additional hydrocarbon and carbon monoxide oxidation during engine warm-up.

Within each car model, individual cars were matched as closely as possible with respect to equipment and calibrations. Compression pressures, compression ratios, spark advance calibrations, and carburetor and EGR flow calibrations were all checked on the new engines before the program began.

Table 1A - Fuel Properties

	Clear Fuel	1/8 MMT Fuel	1/16 MMT Fuel
Specific Gravity at 16°C (60°F)	0.752	0.752	0.753
Lead, g/ℓ	0.002	0.002	0.002
(g/gal)	(0.006)	(0.006)	(0.006)
Reid Vapor Pressure, kPa	60.0	60.0	60.7
(lbs)	(8.7)	(8.7)	(8.8)
Gum, mg/100 mℓ - existent	29.6	42.0	32.0
- after heptane wash	1.2	7.6	1.0
Sulfur, wt %	<0.005	0.005	<0.005
Manganese, g/ℓ	~0	0.034	0.017
(g/gal)	(<0.002)	(0.129)	(0.064)
Octane			
Research octane number	91.4	94.0	92.1
Motor octane number	83.3	84.7	83.5
F.I.A., vol %			
Paraffins	61	62	60
Olefins	6	5	7
Aromatics	33	33	33
Distillation, Evaporation Method			
Initial boiling point, °C	37	37	36
(°F)	(98)	(98)	(96)
10% evap temp, °C	57	57	57
(°F)	(135)	(135)	(135)
20% evap temp, °C	67	68	68
(°F)	(153)	(154)	(154)
30% evap temp, °C	79	80	79
(°F)	(174)	(175)	(174)
50% evap temp, °C	102	102	102
(°F)	(215)	(215)	(215)
70% evap temp, °C	126	126	121
(°F)	(258)	(258)	(250)
90% evap temp, °C	164	166	165
(°F)	(326)	(331)	(329)
End Point, °C	205	200	197
(°F)	(401)	(392)	(387)
Recovery, %	98.6	98.9	98.4
Residue, %	0.9	0.8	0.8
Loss, %	0.5	0.3	0.8

Table 2A - Car Description

	Oldsmobile Cutlasses	Chevrolet Novas
Engine Type	V-8	L-6
Engine Displacement, ℓ	5.7	4.1
(cu in.)	(350)	(250)
Carburetor Barrels	4	1
Transmission Type	Automatic	Automatic
Nominal Compression Ratio	8.5	8.3
Exhaust Emission Controls:		
Type of catalyst	UFB (HN2428-08)	CCM + UFB (HN2428-07)
AIR	No	Yes
EGR	PV	PV, BPM
EFE	No	Yes
Spark Plugs:		
Type	R46SX	R46TS
Gap, mm	2.03	0.89
(in.)	(0.080)	(0.035)
Body Style	4-Door Sedan	4-Door Sedan
Air Conditioning	Yes	Yes

Abbreviations: UFB - underfloor beads
CCM - close-coupled monolith
AIR - air injection reactor
EGR - exhaust gas recirculation
PV - ported vacuum signal
BPM - exhaust back pressure modulation
EFE - early fuel evaporation

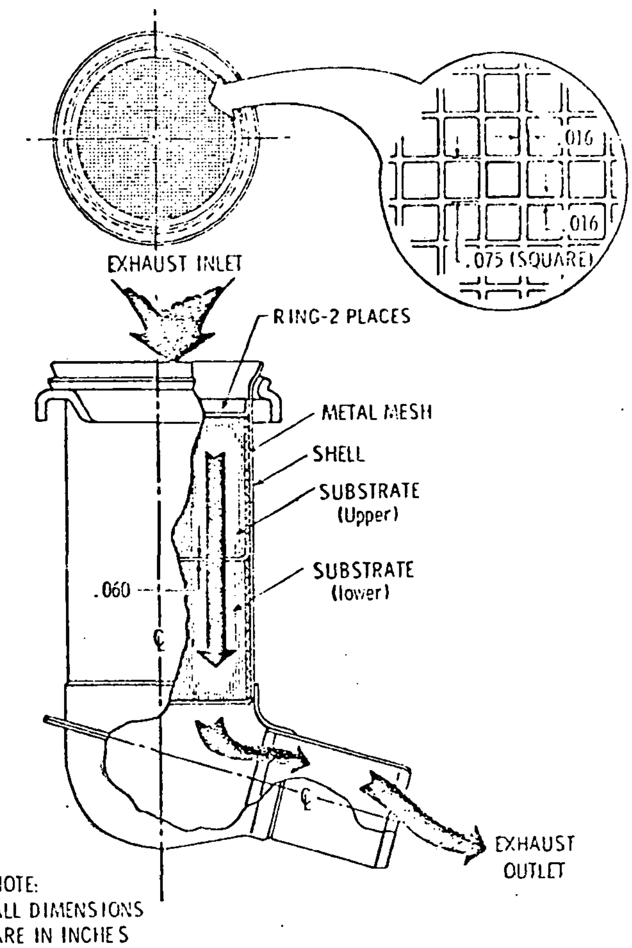

Fig. 1A - Manifold converter

Car numbers R6907 and CH63326 accumulated mileage with Clear Fuel. Cars R6908 and CH63289 used 1/8 MMT Fuel; car CH63291 used 1/8 MMT Fuel during the first portion of the program and 1/16 MMT Fuel during the last portion as will be described in the following

EXPERIMENTAL PROGRAM - Each of four cars accumulated 80 000 km (50,000 miles) on mileage accumulation dynamometers using the assigned fuel and the original set of spark plugs. The other car (CH63291) used 1/8 MMT Fuel for the first 36 000 km (22,000 miles), then the spark plugs were replaced and 1/16 MMT Fuel was used for the next 29 000 km (18,000 miles). The cars were operated for five days each week. Each car was driven for 16 hours and then parked and allowed to cool down for 8 hours every day.

A special driving schedule, designated R007D, was used for mileage accumulation, and the various driving maneuvers are shown graphically in Figure 2A. This schedule was chosen to emphasize freeway speeds of 72 km/h (45 mph) to 113 km/h (70 mph) since many people drive at those speeds, particularly during cross-country vacation trips. In Figure 3A, a distribution of vehicle speeds during the R007D schedule is compared to a distribution of speeds for the AMA schedule which is normally used for mileage accumulation during emission certification tests. The dashed curve in Figure 3A is a speed distribution from a 20-customer survey conducted recently by the General Motors

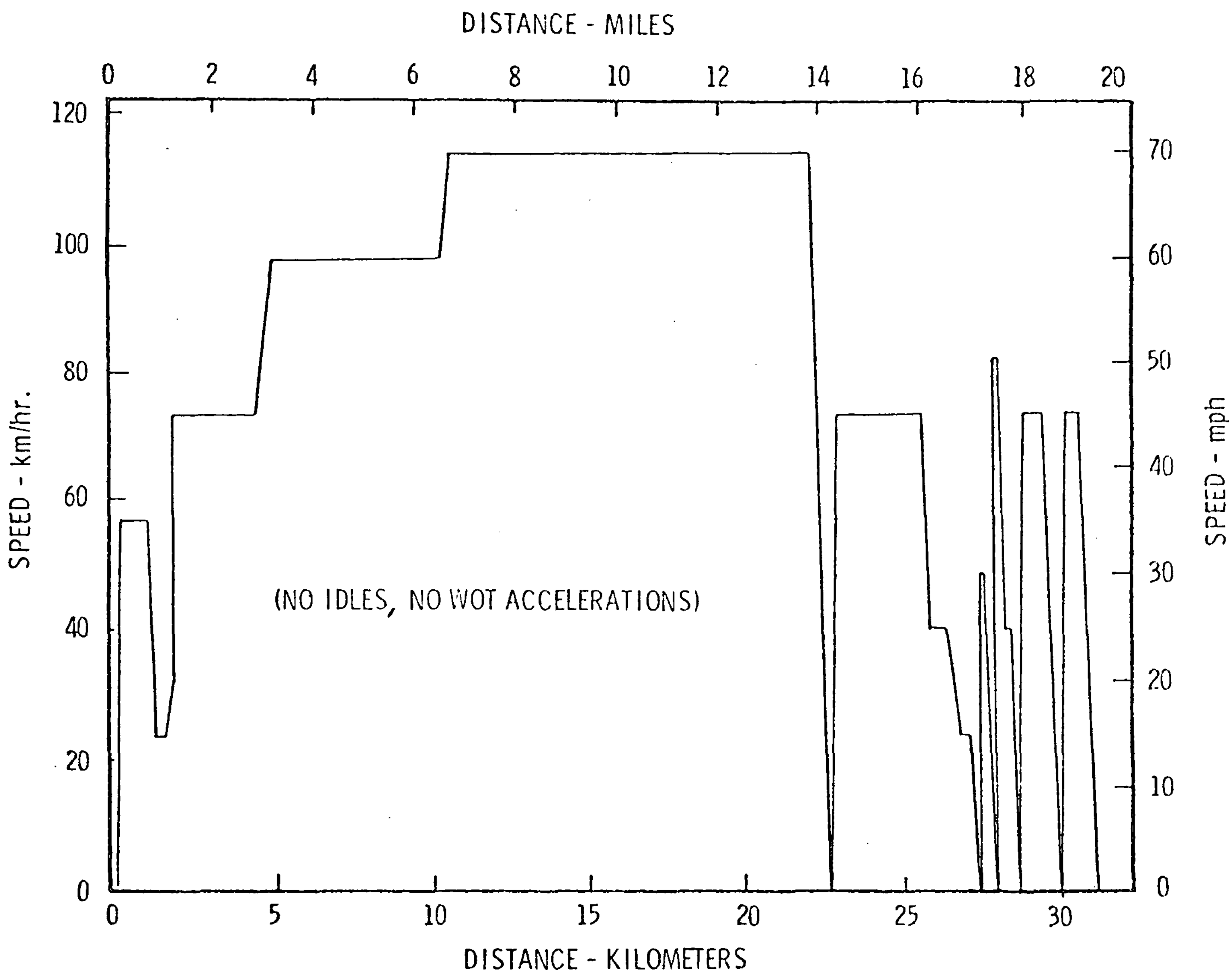

Fig. 2A - Driving events in the R007D mileage accumulation schedule

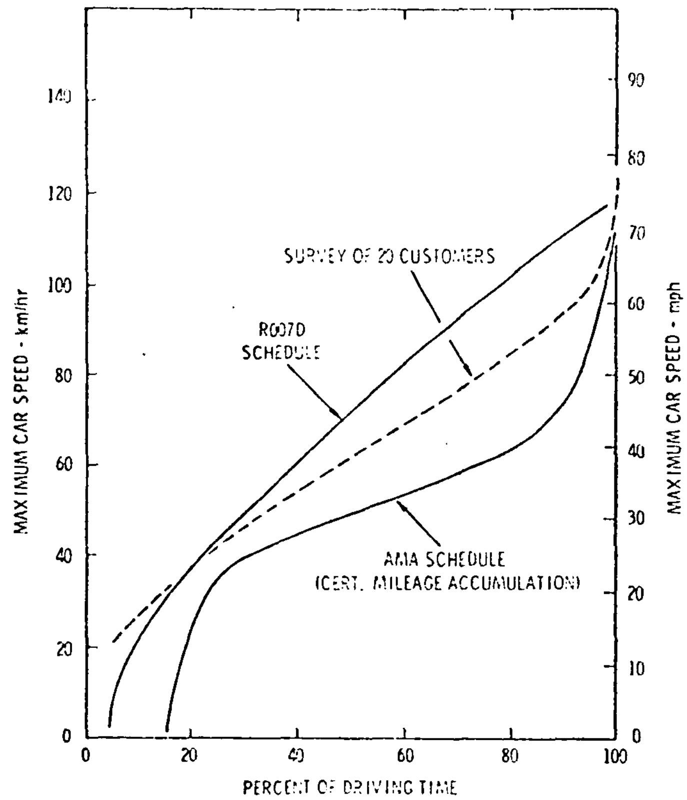

Fig. 3A - Comparison of car speeds during various driving schedules

three distribution curves are 72 km/h (45 mph) for the R007D schedule, 48 km/h (30 mph) for the AMA schedule, and 64 km/h (40 mph) for the 20-customer survey.

During the program, exhaust emissions were measured at 8 000 km (5000 mile) intervals and also whenever a converter plugged. For the Novas, emissions of HC, CO, and NO_x were measured continuously in the exhaust stream ahead of the manifold converter and also at the tail pipe during the Federal exhaust emission test. The next day, emissions were measured between the manifold and underfloor converters and at the tail pipe. Conversion efficiency of the manifold converter was computed by using the engine-out emissions from the first test and the underfloor converter inlet (manifold converter outlet) emissions for the second test. This technique ignores test variability from day to day, but was used because of instrumentation limitations. For the Cutlasses, emissions were measured continuously ahead of the underfloor converter and at the tail pipe during each Federal emission test. All reported data are expressed as composite values calculated from continuous modal measurements of exhaust emissions.

Octane requirements of each car were also measured at 8 000 km (5000 mile) intervals using the CRC E-15 technique (7) and the GMRU reference fuels (11) which represent unleaded gasolines of average sensitivity. During these tests, each car was also checked subjectively for misfire during accelerations.

APCA NOTE-BOOK

Methylcyclopentadienyl Manganese Tricarbonyl: Effect on Manganese Emissions from Vehicles on the Road

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This note describes some measurements of manganese concentrations and manganese emission rates, categorized as to vehicle type, from cars and trucks at two tunnels on the Pennsylvania Turnpike. These measurements were made during the period that methylcyclopentadienyl manganese tricarbonyl (MMT) came into use as an alternative to organo-lead compounds for improving combustion in gasoline engines.

Moran[1] has reviewed several reports, mostly unpublished, dealing with Mn emissions from gasoline engines and vehicles with and without MMT, and has tried to project its effect on environmental Mn levels. The average of the reported emission rates without MMT was ~0.06 mg/km. With MMT, only 4 to 40% (say 20%) of the Mn was emitted. Near-freeway average Mn levels ≈0.25 $\mu g/m^3$ were projected for 100% usage of ⅛ g Mn/gal.

TerHaar, *et al.*[2] have focused on the Mn chemical and physical properties in the exhaust from test cars on a dynamometer. They concluded that some 20% of the Mn consumed would be emitted as particles in the airborne size range, mostly as Mn_3O_4. They found scarcely detectable Mn in the gas phase, with rapid (minutes or less) photolysis to the particulate phase. From these laboratory measurements they predicted 0.05 $\mu g/m^3$ as a median urban area ambient Mn stemming from use of ⅛ g Mn/gal in all gasoline. Subsequently the possibility was debated that levels even that low might significantly catalyze SO_2 oxidation.[3] Moreover, 0.05 $\mu g/m^2$ would be a substantial increase over existing ambient levels (Table 6 of Reference 1).

Clearly one would like to know what the real-world emission rates and concentrations are and how these relate to emission rates and concentrations already existing. The purpose of this note is to offer some information of that nature.

The sites and general methods of the tunnel experiments are described elsewhere.[4-6] Manganese was measured in the tunnel and in the outside air going into it. The tunnel air and traffic fluxes are both known; hence, the mg/km emission rate can be calculated directly from the Mn concentration difference between the tunnel air and outside air. The emission rate so determined includes all of the Mn generated by the vehicle, not just the exhaust emissions. Sampling periods were chosen to span the widest possible range of car/truck ratios. Linear regression of mg/km against the changing traffic composition gives emission-rate estimates resolved as to vehicle type (cars and Diesel trucks), as detailed in Reference 6.

The Mn was determined by collection on absolute particulate filters followed by atomic absorption analysis. Results are summarized in Tables I and II.

Fuel and lubricant samples were collected at all up-road Turnpike service plazas. By the time of the August 1976 experiment, MMT was starting to appear on the market. From August 1976 to July 1977, the use of Mn in unleaded gasoline sold at the Turnpike service plazas had increased, as had also the unleaded share of total gasoline sales at the plazas, giving a 4-fold rise in overall average gasoline Mn (from 4 mg/gal to 16) between the two dates. We found only trace amounts of Mn in the engine lubricants (~1 ppm) or fuels (~1 mg/gal) sold at the plazas, except where MMT had clearly been added.

In general, vehicle-derived Mn concentrations in the tunnel air are ~0.1 $\mu g/m^3$ (Table I). The effect of MMT is evident in the increased Mn emission rate from gasoline-powered vehicles between 1976 and 1977 (Table II; the increase between 5/27/76 and 6/29/77 is significant at a 96% confidence level).

However, only in 1977 does the amount of Mn from gasoline-powered vehicles become comparable with that from Diesel trucks. The dominance of Diesels is the reason why no trend is observed in the Mn concentrations

Table I. Manganese concentrations, $\mu g/m^3$.

	Allegheny Tunnel 7/2/75–7/9/75	Allegheny Tunnel 5/27/76–6/2/76	Tuscarora Tunnel 8/18/76–8/24/76	Tuscarora Tunnel 6/29/77–7/7/77
Tunnel	0.08 (0.06–0.11)	0.13 (0.06–0.21)	0.13 (0.05–0.22)	0.10 (0.05–0.17)
Outside	0.010 (0.003–0.022)	0.009 (0.002–0.015)	0.020 (0.008–0.032)	0.026 (0.014–0.051)
Δ^a	0.07 (0.03–0.09)	0.125 (0.06–0.20)	0.11 (0.04–0.21)	0.07 (0.04–0.10)